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GEORGE OTIS SMITH, DIRECTOR

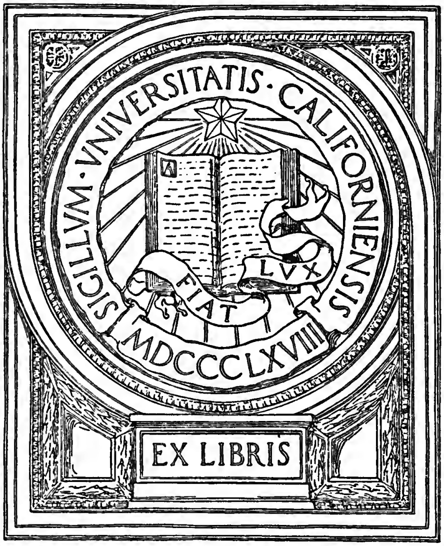
BULLETIN 588

THE CONSTITUTION OF THE NATURAL SILICATES

BY

FRANK WIGGLESWORTH CLARKE

WASHINGTON
GOVERNMENT PRINTING OFFICE
1914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CONTENTS.

THE CONSTITUTION OF THE NATURAL SILICATES.

By Frank Wigglesworth Clarke.

CHAPTER I.

INTRODUCTION.

In the solid crust of the earth the silicates are by far the most important constituents. They form at least nine-tenths of the entire known mass and comprise practically all the rocks except the sandstones, quartzites, and carbonates, and even these exceptions are commonly derivatives of the silicates, which break up under various conditions, yielding new bodies of their own class, together with free silica and limestone. From the geologist's point of view, therefore, the silicates are of fundamental importance, and a study of their inner constitution may be reasonably expected to shed light upon many serious problems. For example, every primitive rock or eruptive mass contains an aggregation of silicates, each one of which is capable of undergoing chemical change in accordance with limitations imposed by the structure of its molecules. When these changes take place secondary compounds, alteration products, are formed, and in time the rock becomes transformed into new substances, quite unlike those which originally existed. A knowledge of the processes which thus occur should be applicable to the study of the rocks and should ultimately render it possible so to investigate a metamorphosed mass as to clearly indicate its origin. These processes are dependent on chemical structure, and the study of this with regard to the silicates is the purpose of the present memoir.

From the standpoint of the chemist the problem under consideration is one of great importance but also of great difficulty. Some of the difficulty is real, some only apparent. At first sight the natural silicates appear to be compounds of great complexity, but this difficulty becomes much less serious after careful examination. Few of the natural silicates exist in even an approximately pure condition; many that seem fresh have undergone traces of alteration; isomorphous mixtures are exceedingly common; and much confusion is due to defective analyses. By multiplied observations these difficulties can be eliminated from the problem, but others yet remain to be disposed of. The organic chemist, to whom most of our knowledge of chemical structure is due, deals mainly with bodies of known molecular weight, which can be measured by the density of a vapor or by cryoscopic methods. To the mineral chemist such knowledge is not available, for the compounds which interest him are neither volatile nor soluble, and their molecular weights can only be inferred. The simplest empirical formula of a silicate is not necessarily its true formula; the latter may be a multiple or polymer of the former; and here we find a difficulty which is at present almost insuperable. Strong evidence can be brought to bear upon this side of the question, but it is only partial evidence and not finally conclusive. The case, however, is by no means hopeless, for even the partial solution of a problem is better than no solution at all. An approximation is some gain, and it is possible so to investigate the constitution of the silicates as to bring many relations to light, developing formulæ which express those relations and indicate profitable lines for future research.

The problem is open to attack along several lines, and various methods of investigation can be brought to bear upon it. First, of course, the empirical formula of each silicate must be definitely ascertained, which involves the discussion of sufficiently numerous analyses and the elimination of possible errors due to impurity, alteration, and isomorphous admixtures. In this work the microscope renders important service to the analyst and makes his results much more certain. By the aid of the microscope many supposed mineral species have been proved to be mixtures, and the problem of the silicates has been thereby simplified. Indeed, the final outcome of such investigation generally indicates, for any given natural silicate, simplicity of composition, and this is what should be expected. These compounds are, as a rule, exceedingly stable salts, whereas complex substances are commonly characterized by instability. The mineral silicates are formed in nature under conditions of high temperature or are deposited from solutions in which many reactions are simultaneously possible, and these circumstances are strongly opposed to any great complications of structure. Furthermore, they are few in number, only a few hundred at most being known; whereas, if complexity were the rule among them, slight variations in origin should produce corresponding variations in character, and millions of different minerals would be generated. That few variations exist is presumptive evidence that only few are possible, and hence simplicity of constitution is reasonably to be inferred. In fact, we find the same small range of mineral species occurring under the same associations in thousands of widely separated localities, a few typical forms containing a few of the commonest metals being almost universally distributed. The longer the evidence is considered, the stronger the argument in favor of simple silicate structures becomes.

The empirical formula of a silicate having been established, its physical properties may next be considered, and of these the crystalline form and the specific gravity are the most important. From identity of form, or complete isomorphism between two species, we infer similarity of chemical structure, and the inferences thus drawn are often of the highest value. On the other hand, dissimilarity of form and identity of composition indicate isomerism, as for example in the cases of andalusite and kyanite, and here again we obtain evidence which bears directly upon the study of chemical constitution. From the specific gravity the so-called molecular volume of a species may be computed, and that datum gives suggestions as to the relative condensation of a molecule in comparison with others of similar empirical composition. For instance, leucite and jadeite are empirically of similar type, but the latter has by far the greater density, together with superior hardness. It is therefore presumably more complex than leucite, and this supposition must be taken into account in considering its ultimate formula.

From what may be called the natural history of a mineral still another group of data can be drawn, relating to its genesis, its constant associations, and its alterability. In this connection pseudomorphs become of the utmost interest and, when properly studied, shed much light upon otherwise obscure problems. An alteration product is the record of a chemical change and as such has weighty significance. The decomposition of spodumene into eucryptite and albite, the transformation of topaz into mica, and many like occurrences in nature are full of meaning with reference to the problem now under consideration. Just here, however, great caution is necessary. Mineralogic literature is full of faulty records regarding alterations, and many diagnoses need to be revised. Pseudomorphs have been named by guesses, based on their external appearance, and often a compact mica has been called steatite or serpentine. Every alteration product should be identified with extreme care, both by chemical and by microscopical methods; for without such precautions there is serious danger of error. Each supposed fact should be scrupulously verified.

Closely allied to the study of natural alterations is their artificial production in the laboratory. The transformation of leucite into analcite, and of analcite back into leucite, is a case in point, and the admirable researches of Lemberg furnish many other examples. Work of this character is much less difficult than was formerly supposed, and its analogy to the methods of organic chemistry renders its results highly significant. Atoms or groups of atoms may be split off from a molecule and replaced by others, and the information so gained bears directly on the question of chemical structure. With evidence of this sort relations appear which could not otherwise be recognized, and these relations may be closely correlated with observations of natural occurrences.

Evidence of the same or similar character is also furnished by the thermal decomposition of silicates, a line of investigation which has been successfully followed by several investigators. Thus garnet, when fused, yields anorthite and an olivine; talc, on ignition, liberates silica; and the prolonged heating of ripidolite produces an insoluble residue having the empirical composition of spinel. All such facts have relevancy to the problem of chemical constitution, and their number could easily be enlarged by experiment. As yet the field has been barely scratched on the surface; upon deeper cultivation a goodly crop may be secured.

The artificial synthesis of mineral species, with the allied study of crystalline slags and furnace products, furnishes still more evidence of pertinent utility. But here again caution is needed in the interpretation of results. A compound may be produced in various ways, and it does not follow that the first method which is successful in the laboratory is the method pursued by nature in the depths of the earth. The data yielded by synthesis are undoubtedly helpful in the determination of chemical constitution, but they furnish only a small part of the proof needed for complete demonstration, and their applicability to geologic questions is extremely limited. For the latter purpose they are only suggestive, not final.

Suppose now that the empirical formula of a silicate has been accurately fixed, and that a mass of data such as I have indicated are available for combination with it. Suppose the physical properties to be determined, the natural relations known, the alteration products observed, its chemical reactions and the results of fusion ascertained; what then? It still remains to combine these varied data into one expression which shall symbolize them all, and that expression will be a constitutional formula. To develop this, the established principles of chemistry must be intelligently applied, with due regard to recognized analogies. The grouping of the atoms must be in accord with other chemical knowledge; they must represent known or probable silicic acids; and any scheme which fails to take the latter consideration into account is inadmissible. Not merely composition, but function also is to be represented, and the atomic linking which leaves that disregarded may be beautiful to see but is scientifically worthless. A good formula indicates the convergence of knowledge; if it fulfills that purpose it is useful, even though it may be supplanted at some later day by an expression of still greater generality. Every formula should be a means toward this end, and the question whether it is assuredly final is of minor import. Indeed, there is no formula in chemistry to-day of which we can be sure that the last word has been spoken.

In the development of constitutional formulæ for the silicates it sometimes happens that alternatives offer between which it is difficult to decide. Two or more distinct expressions may be possible, with the evidence for each so strong that neither can be accepted or abandoned. In such cases nothing can be done but to state the facts and await the discovery of new data, to which, however, the formulæ themselves may give clues. This sort of uncertainty is peculiarly common among the hydrous silicates, and often rises from the difficulty of discriminating between water of crystallization, so called, and constitutional hydroxyl. This difficulty is furthermore enhanced by the common occurrence of occluded water or water in so-called "solid solution," and also by the adsorption of water when a mineral is pulverized for analysis. The serious nature of the latter complication was not recognized until quite recently.

In discriminating between rival formulæ one rule is provisionally admissible. Other things being equal, a symmetrical formula is more probable than one which is unsymmetrical. Symmetry in a molecule conduces to stability; most of the silicates are exceedingly stable; and hence symmetry is to be expected. This rule has presumptive value only, as an aid to judgment, and can not be held rigidly. It expresses a probability but gives no proof. In a problem like that of the silicates, however, even a suggestion of this kind may render legitimate assistance.

There is an extensive literature relative to the constitution of the silicates, which, however, has been well summarized by Doelter,[1] whose summary need not be duplicated here. When necessary suitable reference will be made to the different authorities.

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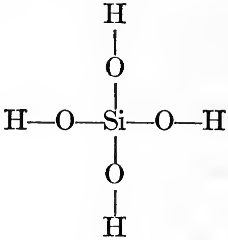
[1] Handbuch der Mineralchemie, vol. 2, pp. 61–109, 1912.

CHAPTER II.

THE SILICIC ACIDS.

If all the silicates were salts of a single silicic acid the problem of their constitution would be relatively simple, but this is not the case. Many silicic acids are theoretically possible, and several of them have representatives in the mineral kingdom, although the acids themselves, as such, are not certainly known. Their nature must be inferred from their salts, and especially from their esters, and this side of the problem is the first to be considered.

As silicon is quadrivalent, its orthoacid is necessarily represented by one atom of the element united with four hydroxyl groups, thus—$Si(OH)_4$, or, structurally:



$$\begin{array}{ccccccccc} & & & & \mathrm{H} & & & & \\ & & & & | & & & & \\ & & & & \mathrm{O} & & & & \\ & & & & | & & & & \\ \mathrm{H} & — & \mathrm{O} & — & \mathrm{Si} & — & \mathrm{O} & — & \mathrm{H} \\ & & & & | & & & & \\ & & & & \mathrm{O} & & & & \\ & & & & | & & & & \\ & & & & \mathrm{H} & & & & \end{array}$$

To this acid, orthosilicic acid, the normal silicic esters and many common minerals correspond. Its normal salts, reduced to their simplest expressions, may be typically represented as follows:

Types.	*Examples.*
$R^{i}_4SiO_4$	$(C_2H_5)_4SiO_4$
$R^{ii}_2SiO_4$	Mg_2SiO_4
$R^{iii}_4(SiO_4)_3$	$Al_4(SiO_4)_3$
$R^{iv}SiO_4$	$ZrSiO_4$

Any silicate in which the oxygen atoms outnumber the silicon atoms by more than four to one, as, for example, the compound Al_2SiO_5, must be regarded as a basic salt.

By elimination of water orthosilicic acid may be conceived as yielding, first, metasilicic acid, H_2SiO_3, and, secondly, the anhydride, SiO_2, thus:

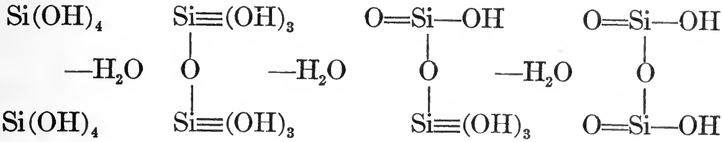
$$Si(OH)_4 \qquad O{=}Si{=}(OH)_2 \qquad O{=}Si{=}O$$

Many salts that correspond to metasilicic acid are known, but no esters have yet been certainly obtained. The esters first described by Ebelmen were supposed to be metasilicates, but all recent investigations have shown them to be ortho compounds, possibly more or less impure. Troost and Hautefeuille, however, have described an ester having the formula $(C_2H_5)_8Si_4O_{12}$, which is a polymer of a metasilicate, but its true nature has not been determined. The simplest formulæ for typical metasilicates are as follows:

Types.	*Examples.*
$R^{i}_2SiO_3$	Na_2SiO_3
$R^{ii}SiO_3$	$MgSiO_3$
$R^{iii}_2(SiO_3)_3$	$Al_2(SiO_3)_3$
$R^{iv}(SiO_3)_2$	$Zr(SiO_3)_2$

The last two examples, $Al_2(SiO_3)_3$ and $Zr(SiO_3)_2$, are salts not actually known, but theoretically possible.

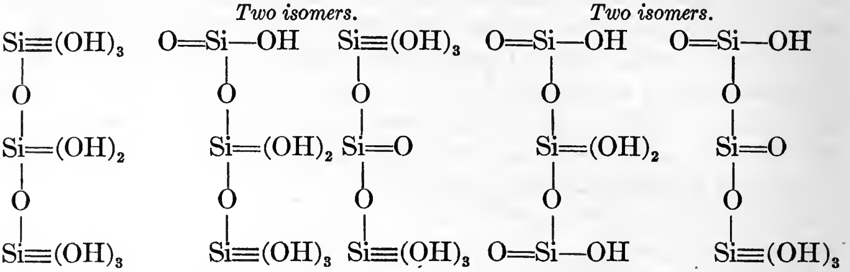
By the coalescence of two molecules of orthosilicic acid and successive elimination, molecule by molecule, of water, a series of disilicic acids may be produced, thus:



The first of these new acids, orthodisilicic acid, $H_6Si_2O_7$, is a sexbasic acid of which several esters are known. It is therefore well established, and a number of minerals appear to be salts of it. The second acid is a polymer of metasilicic acid, dimetasilicic, and its formula is $H_4Si_2O_6$. The third compound, metadisilicic acid, $H_2Si_2O_5$, is represented by no esters, but among its salts are the minerals mordenite, ptilolite, milarite and petalite. By removing the last molecule of water the group Si_2O_4 would remain, a multiple of SiO_2.

By a similar process, that is, by the elimination of water from three or four molecules of orthosilicic acid, a series of trisilicic and quadrisilicic acids may be theoretically developed. These higher acids offer many possibilities for isomerism, just as we know to be the case among the hydrocarbons. For the present, however, only the trisilicic series need be considered, for above that series the long chains of atoms would presumably be unstable. At all events the higher series are at present unnecessary for the interpretation of known minerals.

The trisilicic acids are important and develop as follows:



$$\begin{array}{ccccc}
\begin{array}{c} Si\equiv(OH)_3 \\ | \\ O \\ | \\ Si=(OH)_2 \\ | \\ O \\ | \\ Si\equiv(OH)_3 \end{array} &
\begin{array}{c} O=Si-OH \\ | \\ O \\ | \\ Si=(OH)_2 \\ | \\ O \\ | \\ Si\equiv(OH)_3 \end{array} &
\begin{array}{c} Si\equiv(OH)_3 \\ | \\ O \\ | \\ Si=O \\ | \\ O \\ | \\ Si\equiv(OH)_3 \end{array} &
\begin{array}{c} O=Si-OH \\ | \\ O \\ | \\ Si=(OH)_2 \\ | \\ O \\ | \\ O=Si-OH \end{array} &
\begin{array}{c} O=Si-OH \\ | \\ O \\ | \\ Si=O \\ | \\ O \\ | \\ Si\equiv(OH)_3 \end{array}
\end{array}$$

$H_8Si_3O_{10}$ $H_6Si_3O_9$ $H_6Si_3O_9$ $H_4Si_3O_8$ $H_4Si_3O_8$

Still another acid is possible to complete the series, $H_2Si_3O_7$, to which, however, no known minerals correspond.[1] The first acid of the series, orthotrisilicic acid, has several representatives in the mineral kingdom. The second and third, the trimetasilicic acids, are polymers of metasilicic acid and make, with the similar acids of the previous series, four of the same general formula, nH_2SiO_3. To these acids the four known modifications of magnesium metasilicate may perhaps correspond. The fourth and fifth acids are most important, for they represent the feldspars and appear also in some micas, the scapolites, and several other species. Their isomerism is most suggestive and possibly accounts for such pairs of minerals as orthoclase and microcline, or eudidymite and epididymite, although the latter case is doubtful. The simple name trisilicic acid may be assigned to them, for in abundance their salts outrank all the other acids of the series.

Now, by including the quadrisilicic acids for the moment, ignoring isomers, and tabulating the several compounds,[2] some interesting relations appear:

Dehydration derivatives of orthosilicic acids.

Orthoacids.	First anhydride.	Second anhydride.	Third anhydride.	Fourth anhydride.	Fifth anhydride.
H_4SiO_4	H_2SiO_3	SiO_2			
$H_6Si_2O_7$	$H_4Si_2O_6$	$H_2Si_2O_5$	Si_2O_4		
$H_8Si_3O_{10}$	$H_6Si_3O_9$	$H_4Si_3O_8$	$H_2Si_3O_7$	Si_3O_6	
$H_{10}Si_4O_{13}$	$H_8Si_4O_{12}$	$H_6Si_4O_{11}$	$H_4Si_4O_{10}$	$H_2Si_4O_9$	Si_4O_8.

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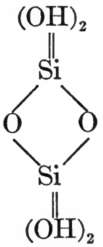
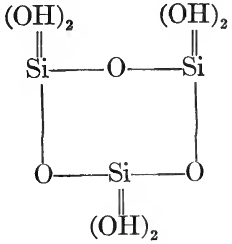
[1] This acid is assumed by Tschermak to be the acid of albite.

[2] This form of tabulation has also been employed by Tschermak, Zeitschr. physikal. Chemie, vol. 53, p. 350, 1905.

This table can be extended indefinitely, with the result that in each vertical column every member below the first differs from the one preceding it by the addition of H_2SiO_3. Furthermore, the first anhydride in each series is either H_2SiO_3 or a multiple thereof. That is, we have a number of homologous series, quite similar to those with which organic chemistry has made us familiar. The final anhydride in every series will be a multiple of SiO_2, and that fact seems to shed some light upon the possible differences between quartz glass, tridymite or cristobalite, and quartz. The commonest associates of quartz are the trisilicate feldspars, to which quartz may be related in respect to its molecular magnitude. Tridymite and cristobalite, with lower specific gravity, are less condensed than quartz and may belong in the disilicic series. The still lighter quartz glass is perhaps the simplest molecule of all, SiO_2. This is hardly more than pure speculation, but the observed relations are certainly suggestive. The denser forms of silica are surely polymers of SiO_2.

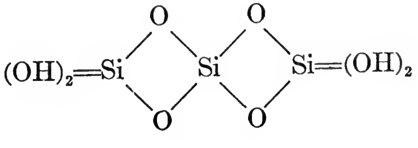
In the foregoing discussion the silicic acids have been represented by "chain" formulæ, analogous to the formulæ of the aliphatic hydrocarbons. But "ring" formulæ of several types are also possible, and some authorities prefer them. For example, one type is as follows:





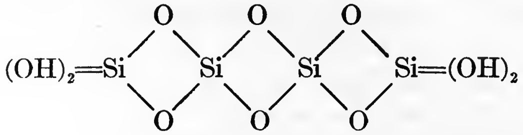
Such formulæ can be extended indefinitely, but no matter how many silicon atoms are introduced into the ring the saturated compound will be a metasilicic acid, nH_2SiO_3. The successive anhydrides will correspond empirically but not structurally to some of the acids of the previous scheme, although none can be equivalent to the higher orthoacids. This limitation makes the ring system less general than the linear or chain system of expressions. Such acids as H_4SiO_4, $H_6Si_2O_7$, and $H_8Si_3O_{10}$ are impossible under it.

By the coalescence of two or more rings, such as is common among the aromatic hydrocarbons, still more complex acids are conceivable, thus:

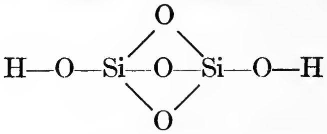


or $H_4Si_3O_8$, isomeric with the important trisilicic acids of the chain series.

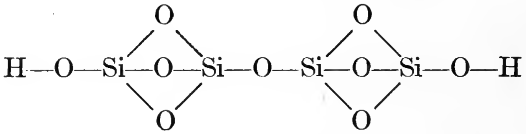
Again,



or $H_2Si_4O_{10}$, a polymer of the disilicic acid $H_2Si_2O_5$, and so on indefinitely. Here again the limitation holds that the acids with a higher oxygen ratio than appears in the formula $H_4Si_3O_8$ are excluded from the scheme. With triple linkings of oxygen only one silicic acid is immediately possible, namely,



or $H_2Si_2O_5$, another isomer of the disilicic acid in the chain series. Two such rings, however, may be linked together by an oxygen atom, thus:



or $H_2Si_4O_9$, an acid which corresponds to no known compounds. All possible acids which appear in the ring formulæ are included in the chain system, at least so far as their empirical formulæ are considered. It is evident, therefore, from what has been already demonstrated, that the chain system is the most complete and general. It is not necessary, in the present state of knowledge, to go beyond it, although this conclusion should only be held tentatively. It is possible that some of the simpler rings may help to interpret some cases of isomerism.[1]

So far, then, there are only a moderate number of silicic acids whose salts appear to need consideration in interpreting the natural silicates. They are:

Orthosilicic acid	H_4SiO_4
Metasilicic acid	H_2SiO_3
Orthodisilicic acid	$H_6Si_2O_7$
Dimetasilicic acid	$H_4Si_2O_6$
Metadisilicic acid	$H_2Si_2O_5$
Orthotrisilicic acid	$H_8Si_3O_{10}$
Trimetasilicic acid	$H_6Si_3O_9$ (two isomers)
Trisilicic acid	$H_4Si_3O_8$ (two isomers)

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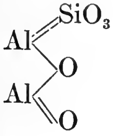
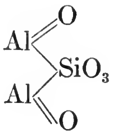
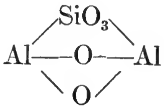
[1] Ring formulæ, like some of those given in the text, are used by Vernadsky, Zeitschr. Kryst. Min., vol. 34, p. 37, 1901.

Many other acids are theoretically possible, and one of them, $H_8Si_4O_{12}$, is perhaps represented by Troost and Hautefeuille's ester, $(C_2H_5)_8Si_4O_{12}$. Salts of such acids may occur in the mineral kingdom, but so far as present evidence goes the probability of their existence is very small.

If the natural silicates were simple normal salts of a few silicic acids the problem of their constitution would not be difficult. But relatively few of the known species are of this description; the greater number are double salts, and even triple replacements are not uncommon. Furthermore, there are acid and basic salts to be interpreted, and the latter class offers the most serious difficulties. A basic metasilicate, for example, may have the same empirical composition as an orthosilicate, so that its ratios, studied apart from other evidence, tell nothing as to the class in which it belongs. For instance, the formula Al_2SiO_5, which represents the composition of three distinct minerals, andalusite, sillimanite, and kyanite, admits of several different structural expressions. As a basic metasilicate it may be written

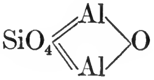






and as an orthosilicate it becomes either

$O{=}Al{-}SiO_4{\equiv}Al$, or



If its molecular weight is a multiple of that indicated by the formula Al_2SiO_5, then the possibilities of isomeric structure become still more complicated. Its composition alone does not give its molecular structure, and other evidence, as shown in the introduction to this memoir, must be brought to bear before the problem can be even approximately solved. This evidence is sometimes available, sometimes not, as will be seen in the systematic discussion of the individual species later.

A similar but less troublesome difficulty arises from the common occurrence of mixed salts, which may represent one or more silicic acids. For example, a well-crystallized silicate on analysis gave the following empirical formula: $Na_2CaAl_4Si_8O_{24}$. At first sight this appears to be a rather complicated metasilicate, but microscopic evidence shows that the mineral is a plagioclase feldspar, and the formula then is resolvable into $2NaAlSi_3O_8 + CaAl_2(SiO_4)_2$, or, in petrographic notation, Ab_2An_1. A trisilicate and an orthosilicate have crystallized together in isomorphous mixture and simulated a metasilicate.

In the interpretation of any silicate, therefore, it becomes important to determine which acid it represents, and that is not often so easy to do as in the case just cited. With some minerals the evidence seems to be very clear, with others it may be misleading. It is only by careful study of a mineral in relation to other species, and with regard to the alterations or chemical reactions of which it is capable, that this phase of the constitutional problem can be solved. A noteworthy attempt in this direction has been made by Tschermak,[1] who in a series of researches has studied the decomposition of silicates by hydrochloric acid and sought to identify the silicic acids so liberated. Tschermak has been followed by Himmelbauer, Baschieri, Silvia Hillebrand, and others. The validity of his method is sharply criticized by Mügge.[2] Some of Tschermak's conclusions are in harmony with the generally accepted views; but others are at least surprising. For example, anorthite and olivine are made to be basic metasilicates; albite is a salt of the acid $H_2Si_3O_7$; and garnet and its congeners are derived from trisilicic acid, $H_4Si_3O_8$. Even if it be admitted that the acids obtained by Tschermak are definite compounds, which has been seriously questioned by Mügge and Van Bemmelen, what evidence is there to show that they represent in any proper sense the original minerals? In the decomposition of the latter many reactions may occur, and the acids finally studied are not necessarily those which were first set free. It is safe to say that the validity of Tschermak's method is not well established.

Siliceous jellies, obtained by decomposing alkaline silicates with acids or by the hydrolysis of $SiCl_4$ or SiF_4, have been studied by many chemists with varying results. Norton and Roth[3] claim to have prepared a definite orthosilicic acid from SiF_4, but the compound lost water steadily on exposure to air. Their memoir contains numerous references to the literature of the subject.

A hasty glance over the entire field of the natural silicates will show, first, that many of them are most easily interpreted as orthosilicates, and, secondly, that by far the greater number are salts of aluminum. As regards both abundance and variety the aluminous silicates outrank all the others, and from the wide range of composition which they exhibit we can obtain clues to their constitution. In other words, they furnish the most evidence, and some of it is of the highest import. Their relations to one another are oftentimes clear and unmistakable, so that the constitution of one salt is the key to that of a second, and thus generalization becomes possible.

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[1] K. Akad. Wiss. Wien Sitzungsber., vol. 112, Abth. 1, p. 355, 1903; idem, vol. 115, Abth. 1, p. 217, 1906; Zeitschr. physikal. Chemie, vol. 53, p. 349, 1905; Centralbl. Mineralogie, 1908, p. 225; Zeitschr. anorg. Chemie, vol. 63, p. 230, 1909; idem, vol. 66, p. 199, 1910.

[2] Centralbl. Mineralogie, 1908, pp. 129, 325; and Van Bemmelen, Zeitschr. anorg. Chemie, vol. 59, p. 225, 1908. See also Serra, R. accad. Lincei Atti, vol. 19, p. 202, 1910.

[3] Am. Chem. Soc. Jour., vol. 19, p. 832, 1897.

The constitution of these aluminous silicates has been studied from various points of view. They may be regarded as ordinary silicates, in which the function of the aluminum is entirely basic, or as salts of complex acids containing aluminum as part of the negative radicle. That is, the existence of alumosilicic acids is assumed and the various minerals are classed as alumosilicates. This mode of interpretation has been much in vogue of recent years but is open to the objection that it is purely hypothetical. Aluminum may so combine with silicic radicles as to form complex ions, but that it does so is quite unproved. Some writers have argued that the aluminum of the silicates is unreplaceable by other basic radicles, and that the compounds in question are thus different in character from the silicates of dyad bases. When, however, andalusite or topaz alters to muscovite, one-half of the aluminum is replaced by the group KH_2, and so the argument breaks down. The term "alumosilicate" may, nevertheless, be used as one of convenience, provided that we remember its limitations. The complex ions may exist, but they should not be taken too strenuously for granted. The fact that alumina combines with silica is alone certain. That the alumosilicates are double salts, with all of the aluminum basis, is just as probable as the alternative hypothesis. A good summary of the diverse views relative to the alumosilicates is given by Doelter.[1] Some of them will be considered later as regards their bearing on individual mineral species.

A novel interpretation of the alumosilicates has recently been put forth by W. and D. Asch,[2] and, as it has received considerable attention, it may be briefly noticed here. The authors have developed what they call the "hexite-pentite theory," in which rings of silicon hydrates are represented as coalescing with similar aluminous rings. These rings, as the terminology indicates, may contain either six or five atoms of silicon or aluminum alternating with oxygen atoms, as in the ring formulæ already considered here, and they have a superficial analogy with the benzene ring of organic chemistry. The silicon hexite acid, $H_{12}Si_6O_{18}$, is evidently a multiple of H_2SiO_3; the aluminum ring is $H_6Al_6O_{12}$, equivalent to diaspore. By the coalescence of four such hexite or pentite rings, either two silicic and two aluminous or three of one to one of the other, the authors develop formulæ for 17 alumosilicic acids, having from 6 to 24 replaceable hydrogen atoms, and with molecular weights ranging between 873 and 1,693. From such complicated acids and their successive anhydrides the alumosilicates are derived. The acids themselves with few exceptions, have no representatives in nature and are purely hypo-

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[1] Handbuch der Mineralchemie, vol. 2, pp. 61-109, 1912.

[2] Die Silicate in chemischer und technischer Beziehung, Berlin, 1911.

thetical. From them, with so many replacements possible an enormous number of salts can be predicated, and isomorphous mixtures, altered or impure minerals, and even bad analyses may easily be given place in the system. Whether, however, silicates of corresponding complexity could exist at the temperatures of even the coolest magma is most questionable. A generalization which does too much may be worse than no generalization at all. Even for such substances as glass the authors of the hexite-pentite theory write structural formulæ.

CHAPTER III.

THE SILICATES OF ALUMINUM.

GENERAL RELATIONS.

A strictly logical investigation of the natural silicates might well begin with those of magmatic origin, for from them all others have been derived. Such a procedure, however, can not be adopted exclusively, for the various compounds, primary and secondary, are connected by so many interlocking relations that neither class should be considered alone. This point is well illustrated by the primary alumosilicates, some of whose derivatives are more suggestive than the original species. In this class the only simple silicate which has so far been crystallized from a molten mixture of silica and alumina is sillimanite, Al_2SiO_5. More complex salts are easily generated from dry fusions, as, for example, nephelite, leucite, and anorthite, and each one is the progenitor of many secondary minerals. The problem of their structural correlation is the problem now in hand.

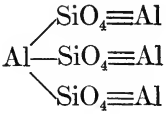
If we consider first the orthosilicates of aluminum one general relation is easily made apparent. By a general relation I do not mean a universal relation, for exceptions are possible, but only that many of the salts are connected by a simple regularity or even a law. To make this clear it is necessary to recognize the fact that aluminum is now properly regarded as a trivalent metal, its formerly supposed quadrivalency being no longer admissible. Formulæ in which aluminum appears as a tetrad are not valid, and ferric iron, which replaces aluminum, follows the same rule. This point has been established by the vapor density and cryoscopic investigations of recent years, and is sustained also by the position of aluminum in the periodic classification of the elements.

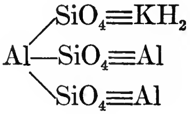
This much admitted, the general relation of which I have spoken is as follows: Many, perhaps all, of the orthosilicates of aluminum are most simply represented as substitution derivatives of the normal salt $Al_4(SiO_4)_3$. To illustrate this rule for present purposes, the following examples will suffice:

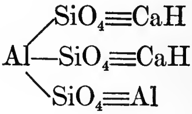
Aluminum orthosilicate	$Al_4(SiO_4)_3$
Eucryptite	$Al_3(SiO_4)_3Li_3$
Nephelite	$Al_3(SiO_4)_3Na_3$
Kaliophilite	$Al_3(SiO_4)_3K_3$
Muscovite	$Al_3(SiO_4)_3HK_2$
Paragonite	$Al_3(SiO_4)_3NaH_2$
Kryptotile	$Al_3(SiO_4)_3H_3$
Andalusite	$Al_3(SiO_4)_3(AlO)_3$
Topaz	$Al_3(SiO_4)_3(AlF_2)_3$

These formulæ express not only the composition of the minerals but also many facts concerning their relations, such as their association, their alteration one into another, and so on. Thus, topaz and andalusite are crystallographically akin; both minerals, as well as others in the series, alter easily into muscovite, and these facts become intelligible in the light of the formulæ given. In the use of the formulæ, however, one possible misconception must be avoided. They express a relationship of constitution but do not imply that nature first generated the normal salt and then actually developed the other compounds from it. To emphasize this point an analogy may be drawn from organic chemistry. Alizarin, derived constitutionally from anthracene, was originally obtained from a glucoside contained in madder root. But nobody supposes that the madder plant took anthracene as a starting point from which to produce the dye. The constitutional or structural derivation is one thing; the natural origin is quite another.

Whether aluminum orthosilicate as such occurs in nature is still a matter of doubt. At all events its existence has not been definitely established. It is theoretically possible, and an artificial hydrate of the formula $Al_4(SiO_4)_3.6H_2O$ has been described by Pukall.[1] As regards its ultimate constitution or chemical structure there is much uncertainty. Its formula can be written structurally in several ways; as, for instance, with each aluminum atom linked with all three SiO_4 groups, or with only one atom so connected. In a sense this problem is analogous to that offered by the benzene ring, prism, or nucleus, a conception of which the utility is fully recognized, in spite of outstanding uncertainties. For practical purposes, that is, for the coordination of known facts, expressions like the following are sufficient:







These expressions indicate the observed replaceability of aluminum atoms by other atoms or groups and have no ulterior significance. So long as their limitations are kept in mind they are useful, but beyond this it would be unreasonable to go. With prolonged discussion and more evidence we may get a deeper insight into the nature of the fundamental molecule; at present, speculation concerning it would be premature. The relations expressed are clear, no matter what others may be revealed in the future. As a working hypothesis, the conception of substitution from a normal salt may be applied to many non-aluminous silicates, as in the magnesian series, the silicates of quadrivalent metals, and so on. These points will be developed in subsequent

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[1] Deutsche chem. Gesell. Ber., vol. 43, p. 2098, 1910.

chapters. For the present we need only to consider the alumosilicates, group by group.

THE NEPHELITE TYPE.

If, now, we start out from the normal aluminum orthosilicate the first and simplest replacement possible is that of a single aluminum atom by three monads, giving a compound of the general formula $Al_3(SiO_4)_3R'_3$. This formula represents several well-known minerals, and I propose to designate it the nephelite type. At first sight it seems to be reducible to the simpler expression $R'AlSiO_4$, but that expression, as will be seen later, does not indicate all the known relations of the group.

The first three representatives of this type are as follows:

Eucryptite.. $Al_3(SiO_4)_3Li_3$
Nephelite.. $Al_3(SiO_4)_3Na_3$
Kaliophilite.. $Al_3(SiO_4)_3K_3$

These species are all hexagonal, are nearly equal in density, and all gelatinize with hydrochloric acid. The second and typical member of the series has been made synthetically, and is then found to have the composition indicated by the formula. The natural nephelite, however, has a composition which is more exactly represented by the complex formula $R'_3Al_3Si_9O_{34}$, in which a little potassium appears among the components of R′, and the silica is in excess of the amount required by theory. The potassium is doubtless due to an isomorphous admixture of kaliophilite, and the excess of silica can be explained by the presence of a salt isomeric with albite and having the composition $Al_3(Si_3O_8)_3Na_3$. This replacement of SiO_4 by Si_3O_8 appears to be common among the silicates, and its recognition clears up many discrepancies. In this case one molecule of the trisilicate commingled with fifteen of the ortho salt will produce the divergence from normal composition shown in the analyses of natural nephelite.

This view of the constitution of nephelite has been adopted by Schaller,[1] and is also favored by Bowen,[2] who has studied the fusion diagram of the system silica, alumina, and soda. In that investigation Bowen found that at about 1,550° nephelite is transformed into a triclinic isomer, a soda anorthite, to which the name carnegieite has been given. Foote and Bradley,[3] however, have advanced a slightly different interpretation of the anomalous composition of natural nephelite, ascribing the excessive silica to "solid solution." These three researches represent the most recent and most conclusive work. Morozewicz[4] has explained the divergent analyses of nephelite by assuming a series of different nephelite molecules, derived from a

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[1] Washington Acad. Sci. Jour., Sept. 19, 1911.

[2] Am. Jour. Sci., 4th ser., vol. 33, pp. 49, 551, 1912.

[3] Am. Jour. Sci., 4th ser., vol. 33, p. 439, 1912.

[4] Acad. Cracovie Bull., 1907, p. 958.

number of alumosilicic acids. That interpretation seems to be no longer tenable. A normal mineral $(Na,K)AlSiO_4$ has been described by Zambonini[1] under the name of pseudonephelite. It is evidently a mixture of nephelite and kaliophilite. The equivalency of these species is also clearly proved by an experiment of Lemberg,[2] who heated nephelite (elæolite) with a solution of potassium silicate and obtained a product having the composition of kaliophilite.

Eucryptite and nephelite both alter with great ease into muscovite, a potassium salt of which paragonite is the sodium equivalent. Furthermore, C. and G. Friedel,[3] by heating finely divided muscovite to 500° in a solution of alkali, obtained nephelite in crystals. From this evidence the formulæ of muscovite and paragonite become directly related to those of the nephelite series, thus:

Nephelite	$Al_3(SiO_4)_3Na_3$
Muscovite	$Al_3(SiO_4)_3KH_2$
Paragonite	$Al_3(SiO_4)_3NaH_2$

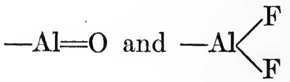
Physically, the two micas have no resemblance to nephelite, being different in form, slightly denser, and refractory toward acids. The relationship is purely one of chemical type, and is established by the fact of alteration from one into another.

Kryptotile, according to Uhlig,[4] is an end member of the mica group. If so, its formula becomes $Al_3(SiO_4)_3H_3$. The claylike mineral leverrierite has apparently the same composition and may be the same compound, and another clay, rectorite, is similar but with one additional molecule of water, which is lost at 110°. The compound may be regarded as an alumosilicic acid, with three replaceable hydrogen atoms, although such an interpretation of it is not necessary.

Through muscovite a connection is recognizable between the foregoing species and the two minerals andalusite and topaz, whose simplest formulæ, tripled, may be written as follows:

Topaz	$Al_3(SiO_4)_3(AlF_2)_3$
Andalusite	$Al_3(SiO_4)_3(AlO)_3$

Here we encounter the evidently univalent atomic groups



$$—Al=O \text{ and } —Al\begin{matrix}\diagup F\\ \diagdown F\end{matrix}$$

both of which play an important part in various other minerals. The two species, topaz and andalusite, are closely allied crystallographically. They have sensibly identical molecular volumes, and both undergo alteration into muscovite mica.[5] In topaz, as shown by the

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[1] Chem. Soc. Jour., vol. 98, pt. 2, p. 1078, 1910. Abst. from Accad. Napoli Rend., 1910.

[2] Deutsche geol. Gesell. Zeitschr., vol. 37, p. 966, 1885.

[3] Min. Soc. Bull., vol. 13, p. 183, 1890.

[4] Zeitschr. Kryst. Min., vol. 47, p. 215, 1910.

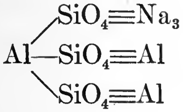
[5] For a good example of this alteration see Clarke and Diller, U. S. Geol. Survey Bull. 27, p. 9, 1886.

investigations of Penfield and of Jannasch, hydroxyl commonly replaces a part of the fluorine, hydroxyl and fluorine being clearly isomorphous. The formula given is that of normal topaz, entirely free from alteration.

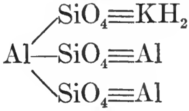
Obviously the formula of muscovite is the key to all other formulæ in this group of silicates. Its minimum molecular weight is represented by the expression $Al_3KH_2Si_3O_{12}$ and to that the others must conform. The general formula $Al_3(SiO_4)_3R'_3$ is the lowest possible, and the formula $Na_2Al_2Si_2O_8$, which is often assigned to nephelite, is too small. It may represent the isomeric carnegieite, which being stable at high temperatures is perhaps molecularly less condensed than nephelite. But of this there is no clear evidence. The tripled formulæ are also sustained by an experiment of Silber,[1] who heated an artificial nephelite silicate in a sealed tube with a solution of silver nitrate and replaced one-third of the sodium by silver; that is, one of the three sodium atoms seems to be differently combined from the others. This substitution can be expressed structurally in several ways, but its consideration must be deferred until later. Nephelite yields some zeolitic derivatives, especially hydronephelite and natrolite, but their discussion belongs to another section of this chapter.

To sum up, we have now eight definite species represented by the fundamental type $Al_3(SiO_4)_3R'_3$, the first substitution from the hypothetical normal orthosilicate of aluminum, and these compounds may be divided into three subtypes as follows:

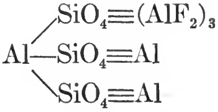
Nephelite.



Muscovite.



Topaz.



symbols which clearly indicate the known chemical relations between the several minerals. In six of the eight examples the simplest possible formulæ have been tripled, for otherwise the relationships which exist could not be structurally shown. The correctness of this procedure will appear still more definitely in the consideration of the groups which follow.

The species sillimanite is isomeric with andalusite, but the structural character of the isomerism is not clear. The two species have nearly the same molecular volumes, and presumably the same molecular weights, but a third isomer, kyanite, is much denser and therefore not so easily correlated with the others. It is commonly regarded as a basic metasilicate, although that is not its only conceivable structure. It is easy to write constitutional formulæ for all these minerals, but they would be of little real significance except in so far as they repre-

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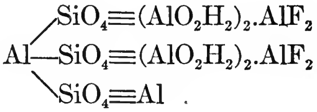
[1] Deutsche chem. Gesell. Ber., vol. 14, p. 941, 1881.

sented possibilities. Sillimanite is the most stable compound of the three, and the only one which has been obtained magmatically. At high temperatures kyanite and andalusite are transformed into sillimanite.[1] Structural formulæ for andalusite and kyanite have been proposed by Zulkowski,[2] but they are based upon the minimum molecular weight of Al_2SiO_5 and are therefore inadmissible.

THE GARNET TYPE.

By this title I propose to designate the second series of derivatives from the normal salt, $Al_4(SiO_4)_3$, in which two atoms of aluminum have been replaced. The general formula of the type obviously is $Al_2(SiO_4)_3R'_6$, and in this series bivalent elements or radicles frequently appear. In lagoriolite, an artificial soda garnet,[3] $R'_6=Na_6$; in prehnite $R'_6=Ca_2H_2$; and in normal garnet and epidote $R'_6=3R''$. There are, therefore, three subtypes to consider—one in which all the replacing atoms are univalent, one in which all are bivalent, and one intermediate between the other two.

Under the first subtype two species may be definitely placed, namely, lagoriolite, $Al_2(SiO_4)_3Na_6$, and zunyite, which is more complicated. In zunyite R'_6 is composed of the univalent radicles $—Al{=}F_2$, $—Al{=}Cl_2$, and $—Al{=}(OH)_2$, but the species has been found in only one locality, and needs further study. At present, if we unite the chlorine in it with the fluorine, it may be provisionally represented by the expression



$$Al\begin{array}{l} \diagup SiO_4\equiv(AlO_2H_2)_2.AlF_2 \\ —SiO_4\equiv(AlO_2H_2)_2.AlF_2 \\ \diagdown SiO_4\equiv Al \end{array}$$

This formula expresses the facts which are now available but is not conclusive. Its isometric character, however, helps to connect zunyite with the garnet and sodalite groups, as has been shown by Brögger.[4]

In the second subtype, when R'_6 is partly composed of bivalent and partly of univalent atoms, two species may be placed, thus:

Prehnite	$Al_2(SiO_4)_3Ca_2H_2$
Biotite	$Al_2(SiO_4)_3Mg_2HK$

Possibly the tetragonal sarcolite, which has the general formula of a garnet with the lime partly replaced by soda, may fall here also, but the analyses of this mineral are unsatisfactory, and its relations are

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[1] Vernadsky, Soc. Min. Bull., vol. 12, p. 447, 1889; vol. 13, p. 256, 1890.

[2] Monatsh. Chemie, vol. 21, p. 1086, 1900.

[3] See Morozewicz, Min. pet. Mitt., vol. 18, p. 147, 1898-99. The formula here given to lagoriolite is that of the ideally pure mineral. The actual product contains a notable admixture of the corresponding lime compound.

[4] Zeitschr. Kryst. Min., vol. 18, p. 209, 1891.

still uncertain. Biotite will be more fully considered in the section devoted to the mica group.

Under the third subtype of this series we find the garnet group itself, together with epidote and several related species. The sodalite group is also akin to garnet and to the second subtype and will be considered in this connection a little later. The generic term garnet covers several species, all isometric and strictly isomorphous, in which magnesium, calcium, and ferrous iron replace one another, and chromium, aluminum, and ferric iron are also equivalent terms. Thus we have:

Grossularite	$Al_2(SiO_4)_3Ca_3$
Pyrope	$Al_2(SiO_4)_3Mg_3$
Almandite	$Al_2(SiO_4)_3Fe''_3$
Spessartite	$Al_2(SiO_4)_3Mn_3$
Andradite	$Fe_2(SiO_4)_3Ca_3$
Ouvarovite	$Cr_2(SiO_4)_3Ca_3$

To these may be added schorlomite, a garnet in which titanium occurs both as part of the acid, that is, with TiO_4 replacing SiO_4, and also as Ti''' among the triad bases, equivalent to aluminum. The monoclinic partschinite, isomeric with spessartite, also falls into this group.

The several species of garnet occur in a great variety of isomorphous mixtures and some of them contain small quantities of alkalies, due to the presence of compounds like lagoriolite.[1]

In the epidote group several species appear, one, zoisite, being orthorhombic, whereas the others are monoclinic. These species are characterized by the bivalent group of atoms $=Al—OH$ or $=Fe—OH$, thus:

Zoisite	$Al_2(SiO_4)_3Ca_2(AlOH)$
Epidote *a*	$Al_2(SiO_4)_3Ca_2(AlOH)$
Epidote *b*	$Fe_2(SiO_4)_3Ca_2(FeOH)$
Piedmontite	$(Al,Mn)_2(SiO_4)_3Ca_2(AlOH)$
Allanite	$(Al,Ce,Fe)_2(SiO_4)_3(Ca,Fe)_2(AlOH)$
Hancockite	$Al_2(SiO_4)_3(Ca,Pb,Sr)_2(FeOH)$

or, in general, as compared with garnet,

Garnet	$R'''_2(SiO_4)_3R''_3$
Epidote	$R'''_2(SiO_4)_3R''_2(R'''OH)$

A chromium epidote, "tawmawite," containing 11.16 per cent of Cr_2O_3 has also been described.[2]

The facts that garnet alters into epidote and that the two minerals are often associated give emphasis to the formulæ.

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[1] For elaborate studies of the garnet group see Brögger and Bäckström, Zeitschr. Kryst. Min., vol. 18, p. 209, 1891; Weinschenk, idem, vol. 25, p. 365, 1896; Uhlig, Naturh. Ver. preuss. Rheinl. u. Westfalens, Verh., vol. 67, pt. 2, p. 307, 1910; and Seebach, Centralbl. Mineralogie, p. 774, 1906.

[2] See Bleeck, India Geol. Survey Records, vol. 36, p. 254, 1907–8.

Although garnet as a rule is unattacked by acids, and epidote is only in part decomposable, both species are so broken up by strong ignition as to be readily acted upon by hydrochloric acid, with separation of gelatinous silica. According to Doelter and Hussak,[1] garnet yields upon fusion sometimes anorthite and an olivine; or meionite, augite, and olivine; or melilite and anorthite; and occasionally spinel. Epidote, says Doelter,[2] yields lime-augite and anorthite, and prehnite behaves like garnet. These facts are interesting, but they give no direct information regarding chemical structure. By fusion the molecules of a silicate are broken down, and on cooling the melt a complete rearrangement of the atoms may take place, although not necessarily. When calcium alumosilicates are fused they may, as in the case of anorthite, recrystallize unchanged, or they may solidify as compounds having little or no structural relations to their progenitor. When, however, silicates are broken down by mere calcination and without fusion the reaction may be highly instructive. Examples of this kind will be noted later.

In the four species sodalite, haüynite, noselite, and lazurite we have a group of minerals which Brögger has classified as alkali garnets.[3] Like garnet, they are all isometric, and they are characterized by the presence of the bivalent groups $=Al-Cl$, $=Al-SO_4-Na$, and $=Al-S-S-S-Na$. There are also artificial products, ultramarines, in which the groups $=Al-S-S-Na$ and $=Al-S-Na$ appear. By adopting Brögger's formulæ, which are preferable to those formerly proposed by myself,[4] these species may be written as follows:

Sodalite	$Al_2(SiO_4)_3Na_4(AlCl)$
Haüynite	$Al_2(SiO_4)_3Na_2Ca(AlSO_4Na)$
Noselite	$Al_2(SiO_4)_3Na_4(AlSO_4Na)$
Lazurite	$Al_2(SiO_4)_3Na_4(AlS_3Na)$

They fall therefore properly under the second subtype, but are considered at this point on account of their analogies with garnet.

The formulæ just assigned to these minerals represent, of course, the ideally pure compounds, which rarely, if ever, occur in nature. The four species are all evidently derived from nephelite, with which sodalite is commonly associated, and their composition varies in the same manner as that of the parent mineral. Like nephelite, sodalite yields natrolite, hydronephelite, and muscovite by alteration. Furthermore, C. and G. Friedel,[5] on heating powdered muscovite with soda solution and sodium chloride at a temperature of 500°, obtained

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[1] Allg. chem. Mineralogie, p. 182, 1890.

[2] Idem, p. 183.

[3] Brögger and Bäckström, Zeitschr. Kryst. Min., vol. 18, p. 209, 1891.

[4] U. S. Geol. Survey Bull. 42, p. 38, 1887.

[5] Soc. min. Bull., vol. 13, p. 183, 1890.

sodalite artificially, although nephelite was probably first formed as an intermediary, and the two species were commingled in the product.

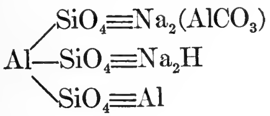
The two hexagonal species, cancrinite and microsommite, are also, like sodalite, undoubtedly derivatives of nephelite, but their formulæ are rather uncertain. At Litchfield, Maine, cancrinite often occurs in intimate mixture with nephelite (elæolite). A cancrinite described by Zambonini[1] corresponds very closely to a mixture of nephelite and the compound $Al_2(SiO_4)_3Na_3Ca(AlCO_3)$.

In its purest varieties cancrinite approximates to the formula $Al_2(SiO_4)_3Na_4H(AlCO_3)$, in which a little soda is replaced by lime, and the univalent group $—Al=CO_3$ may be partly substituted by $—Al=SiO_3$. Microsommite, according to the published analyses, varies widely in composition, invariably containing potassium and having a notable proportion of chlorine and SO_3 among its constituents. If, however, we assume in it the univalent radicles $—Al=Cl_2$ and $—Al=SO_4$, its composition reduces easily to the form $Al_2(SiO_4)_3(NaK)_3Ca(Al(SO_4Cl_2))$, like cancrinite, both species having then the composition of the general type $Al_2(SiO_4)_3R'_6$. The theory as proposed, then, assumes univalent complex radicles for cancrinite and microsommite, and bivalent radicles for the sodalite group, thus:

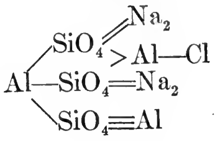
In cancrinite group.	*In sodalite group.*
$—Al=Cl_2$	$=Al—Cl$
$—Al=SO_4$	$=Al—SO_4—Na$
$—Al=CO_3$	$=Al—S_3—Na$
$—Al=SiO_3$	

and the typical structures are as follows:

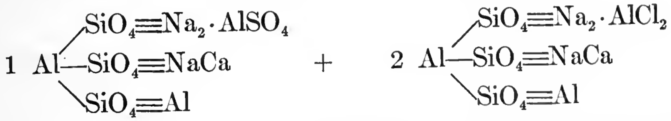
Cancrinite.



Sodalite.



The best analyses of microsommite give very nearly



with nearly half the sodium replaced by potassium; the radicle $AlCO_3$ is also sometimes present.

There are arguments both for and against these formulæ and the peculiar univalent and bivalent radicles assumed in them. The assumption of a group $—Al=SiO_3$, equivalent to and replacing

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[1] Appendice alla mineralogia vesuviana, p. 35.

$—Al{=}CO_3$, is clearly suggested by the experiments of Lemberg,[1] who by the action of sodium silicate solution upon elæolite, obtained a compound which he designates as a cancrinite containing Na_2SiO_3 in place of Na_2CO_3. By similar reactions with sodium carbonate he produced a substance having the composition of true cancrinite. Hence, whatever the ultimate molecular structure of cancrinite may be, we are amply justified in assuming in it the replaceability of CO_3 by SiO_3.

These experiments fairly represent a large number of like kind which are due to Lemberg, and which are recorded in his papers. Some of these will be cited later, but a reference to the work of his colaborer,[2] Thugutt, is in place at this point. Starting from a hydrated nephelite, artificially prepared from kaolin, Thugutt succeeded in producing a large series of compounds analogous to sodalite, in which the original silicate had taken up, at moderately high degrees of heat and pressure, various other salts of sodium, such as the chlorate, selenate, formate, oxalate, and so on. These compounds, however, are all hydrated, and so differ from the natural minerals of the sodalite group, and they are regarded by Thugutt as formed by molecular union. Following Lemberg, he regards sodalite as a molecular compound of nephelite with sodium chloride, and taking his series of compounds throughout, he looks upon the sodium salts which have been added to the fundamental silicate as equivalent in function to water of crystallization. In favor of this view he cites many arguments, some of which are entitled to considerable weight. Thus, when sodalite is ignited $NaCl$ is driven off, whereas if the chlorine were united with aluminum $AlCl_3$ should be expelled. Similarly, by the action of water alone, sodium chloride can be split off from the sodalite molecule, thus indicating a looser form of union than the proposed structural formulæ show.

But what is molecular union? To this question there is no satisfactory answer, and even in the case of water of crystallization the term is only a confession of ignorance. Unless we assume the existence of two kinds of chemical union, it means merely that the structural linking is unknown, and that the problem is laid on one side, conveniently labeled for future reference. The constitutional formulæ here adopted for sodalite and cancrinite are intended to give a provisional solution of the problem in their particular cases and to express the genetic relationships with nephelite on the one hand and the crystallographic analogy with garnet on the other. The objections to them raised by Thugutt are serious but not absolutely conclusive. When sodium chloride is split off from sodalite the mechanism of the reaction is

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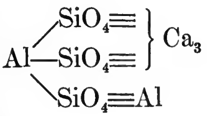
[1] Deutsche geol. Gesell. Zeitschr., 1885, p. 962.

[2] Mineralchemische Studien, Dorpat, 1891. See also Thugutt on cancrinite, Neues Jahrb., 1911, p. 25. Zambonini (Contributo allo studio dei silicati idrati, Napoli, 1908) regards cancrinite as a mixture of silicates, with all the water extraneous—that is, not essential to the molecules. On the sodalite group see also Silvia Hillebrand, K. Akad. Wiss. Wien Sitzungsber., vol. 119, p. 775, 1910.

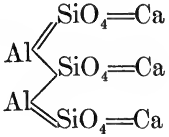
quite unknown, and the relative affinities in the molecule are quite unstudied. Until these are understood the objections raised by Lemberg, Thugutt, and others are not fatal. Furthermore, the presence of a group =Al—Cl does not imply, as Thugutt supposes, the splitting off of $AlCl_3$ by heat. To effect such a decomposition three molecules of sodalite would have to be broken up, and there is no probability that such a disintegration would occur. At all events the formulæ proposed fulfill a definite purpose, even though they are not finally established. They express known relations but not necessarily all the relations which the future may reveal. The facts that the sodalite-cancrinite minerals are derivable from nephelite and that nephelite is again derivable from them are unquestionable.

The question of the molecular structure of a typical garnet, $Al_2(SiO_4)_3Ca_3$, remains to be considered.[1] If it is regarded as a derivative of the normal salt $Al_4(SiO_4)_3$ it may be written in at least two ways, thus:

1.

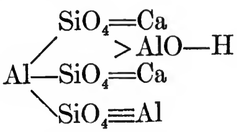


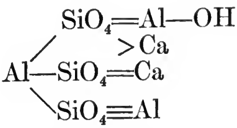
2.



That is, isomerism is possible, and of the two species, partschinite and spessartite, one may belong to one type and the other to the other In the first expression there is still a replaceable atom of aluminum, but in the second expression none; in the first at least one calcium atom must link two SiO_4 groups, whereas in the other no such linkage occurs; and these facts may be connected with others. For example, garnet alters into mica, and the mica group, as will be seen later, contains members in which the third aluminum atom is replaced. This points at once to the first type of formula as preferable, and the alterability of garnet into epidote brings the latter mineral into the same category.

Zunyite and sodalite, being isometric, should also follow garnet, but derivatives of the second type are theoretically possible and may exist. Even under the first type alone isomerism is conceivable, and the orthorhombic zoisite may be contrasted with the monoclinic lime epidote as follows:





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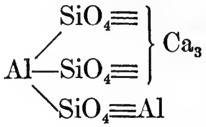
[1] Tschermak (K. Akad. Wiss. Wien, Sitzungsber., vol. 115, p. 217, 1906) regards garnet, epidote, zoisite, and prehnite as salts of the acid $H_4Si_3O_8$, but his formulæ do not well show the relations of these minerals to other species.

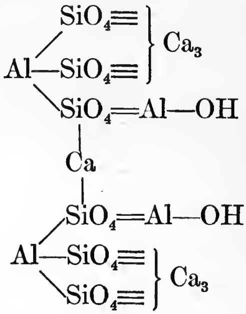
even though we can not assign either species to either formula definitely. My object here is merely to show that the formulæ have properties by virtue of which they are able to express known differences.

Additional evidence for the formula assigned to garnet is supplied by the composition of vesuvianite, which is most simply represented by the coalescence of two garnet molecules with partial hydration, thus:

Garnet.



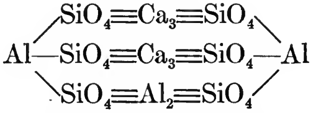
Vesuvianite.



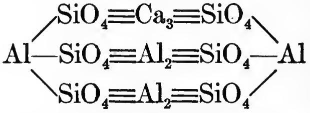
The formula agrees well with many analyses of vesuvianite, but actually, as with other species, its composition varies. About one-seventh of the calcium is commonly replaced by magnesium, and in some varieties boron, presumably in the group =B—OH, replaces in part the corresponding aluminum radicle.[1] Fluorine is also often present in small amount as the equivalent of hydroxyl. In short, a variety of isomorphous replacements or comminglings are possible without affecting the essential structure as shown by the formula. Such replacements are too well known to need detailed discussion here.

The true molecular weights of silicates, however, are unknown, and it is therefore conceivable that the formulæ of garnet and epidote should be doubled. These minerals and vesuvianite have nearly the same specific gravities, 3.3 to 3.5, for the purely calcic varieties. The specific gravities in the cancrinite-sodalite group, on the other hand, are about a unit lower, a fact which favors the simpler, less-condensed molecular structure. On doubling the formulæ of garnet and epidote the following comparison with vesuvianite and anorthite is interesting:

Garnet.



Anorthite.



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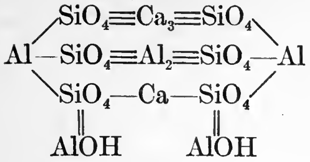
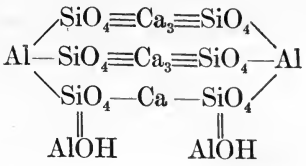
[1] On boron in vesuvianite see Wherry and Chapin, Am. Chem. Soc. Jour., vol. 30, p. 1684, 1908. Weingarten (Centralbl. Mineralogie, 1902, p. 726) represents the mineral by the formula $AlOH{=}Si_2O_7{=}Ca_2$. In the former edition of this memoir, U. S. Geol. Survey Bull. 125, vesuvianite was given the formula $Al_2(SiO_4)_5R_6.AlOH$. See also U. S. Geol. Survey Bull. 262, p. 72, 1905, for variations in the present formula.

Epidote.

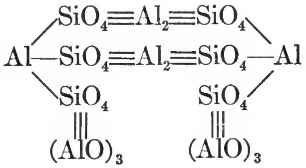


Vesuvianite.



In these new formulæ the essential character of the former expressions is unchanged, but the presumably greater condensation is indicated, with the derivation from two molecules of aluminum orthosilicate instead of from one. They are also sustained by the facts that garnet, epidote, vesuvianite, scapolites, and in some localities anorthite often occur in limestones as products of contact metamorphism; that vesuvianite alters into garnet, garnet into epidote and scapolite, and that all four minerals alter into micas and the magnesian varieties into chlorites also. The species are connected constitutionally and genetically, the analogies connecting them are remarkably suggestive and complete, and the formulæ here proposed render those analogies intelligible. In the Swedish "mangan-idocrase" a salt occurs which is doubtless the vesuvianite equivalent of spessartite, but the compound in a pure state is unknown.

Kyanite, an isomer of andalusite, but of much higher specific gravity, may perhaps be represented as a basic member of the garnet series, although it is morphologically very different. The formula



expresses this relation and also its comparative instability. Both kyanite and andalusite, at very high temperatures, are transformed, with disengagement of heat, into a third isomer, sillimanite,[1] which probably has the simplest formula of the three. This, however, is so purely hypothetical that it would be useless to discuss the several species further.

Two more species, melilite and gehlenite, which, like vesuvianite, are tetragonal, may perhaps be best considered now. Both species are very variable in composition, and neither seems to admit of one definite formulation. They appear to be mixed silicates, like the intermediate plagioclase feldspars and scapolites, but the end members of each series are difficult to identify. An artificial silicate recently obtained by Shepherd and Rankin,[2] in the Geophysical

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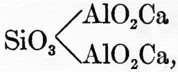
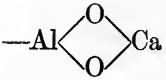
[1] See Vernadsky, Soc. Min. Bull., vol. 12, p. 447, 1889; vol. 13, p. 256, 1890.

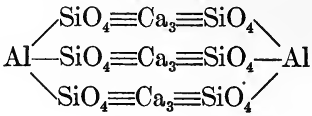
[2] Private communication.

Laboratory of the Carnegie Institution, is probably one end of the gehlenite series and has the formula $Al_2Ca_2SiO_7$, which is that of a basic metasilicate. Structurally it can be written



$$SiO_3 \begin{cases} AlO_2Ca \\ AlO_2Ca, \end{cases}$$

in which the basic radicle  is analogous to the more familiar $—Al{=}(OH)_2$. The other end of the series is probably a silicate of the vesuvianite type,



in which the three replaceable aluminum atoms of the normal orthosilicate are substituted by calcium. If this supposition is correct we have the following complete series:

$Al_6(SiO_4)_6Ca_3$, anorthite.
$Al_4(SiO_4)_6Ca_6$, garnet.
$Al_2(SiO_4)_6Ca_9$, in gehlenite.

In the Mexican gehlenite analyzed by Wright [1] there is an approximation to Shepherd and Rankin's silicate, namely, eight molecules of that compound commingled with one of the other. The comparison is as follows:

	Found.	Reduced.	Calculated.
SiO_2	26.33	26.69	26.51
TiO_2	.03		
Al_2O_3	27.82	29.12	28.98
Fe_2O_3	1.43		
FeO	.50	44.19	44.51
MnO	.01		
MgO	2.44		
CaO	39.55		
Na_2O	.21		
K_2O	.10		
H_2O	1.85	....	....
	100.27	100.00	100.00

The second column is recalculated to 100 per cent after uniting iron with alumina and recomputing the other bases to their equivalent in

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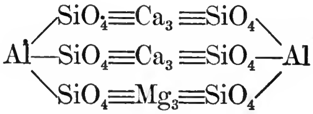
[1] Wright, F. E., Am. Jour. Sci., 4th ser., vol. 26, p. 545, 1908.

lime. Other gehlenite analyses reduce equally well but with much larger proportions of the orthosilicate compound. The Orawitza gehlenite, for example, is very nearly

$$2\ Al_2Ca_2SiO_7 + 1\ Al_2Ca_9Si_6O_{24}.$$

This commingling of an orthosilicate with a very basic metasilicate is not easy to explain, but it seems to fit the actual evidence. It is furthermore sustained by an observation of Cathrein,[1] who has reported pseudomorphs after gehlenite of fassaite, a metasilicate, and grossular garnet. The formula commonly assigned to gehlenite, $Ca_3Al_2Si_2O_{10}$, is inadmissible.

In gehlenite the oxygen is always in excess of the orthosilicate ratio, but in melilite the reverse is generally true. The Vesuvian melilites agree nearly with Groth's formula, $R_6'' R_2''' Si_5O_{19}$, but the mineral from other localities exhibits quite different ratios. An artificial "melilite" obtained by Bodländer[2] from Portland cement is very nearly



as the following comparison shows:

	Found.	Reduced.	Calculated.
SiO_2	37.96	38.63	39.22
Al_2O_3	9.46	11.51	11.11
Fe_2O_3	2.93		
MgO	12.77	12.99	13.07
CaO	34.75	36.87	36.60
K_2O	1.53		
Na_2O	.64		
	100.04	100.00	100.00

Other melilites seem to be mixtures of this type of compound with the corresponding trisilicates—that is, with Si_3O_8 in place of SiO_4, but the evidence is not conclusive. Such mixtures are found in the feldspar, scapolite, and mica groups and are well known. Just as the calcic anorthite crystallizes with the sodic albite so probably in melilite two compounds, one calcic or magnesian, the other alkaline, replace each other isomorphously. Gehlenite and melilite, how-

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[1] Min. pet. Mitt., vol. 8, p. 408, 1886–87.

[2] Neues Jahrb., 1892, vol. 1, p. 53.

ever, seem to have one end compound in common, and that compound belongs in the anorthite-garnet series as already shown. Its synthesis in the pure state is yet to be effected.

Whether the formulæ here proposed are true or not they are useful for purposes of correlation. They are, moreover, emphasized by an experiment made by Lemberg,[1] who has shown that gehlenite, when heated to 200° with a solution of potassium carbonate, gives calcium carbonate and a product having the composition of a potash mica, whereas similar treatment with sodium carbonate converts the mineral into cancrinite. Gehlenite, garnet, cancrinite, and muscovite are therefore related to one another, and this fact is expressed by the formulæ proposed. Furthermore, at Orawitza, in the Banat, gehlenite is found in rolled pebbles containing grains of vesuvianite, a fact which indicates a common genesis for both minerals.

An alternative interpretation of the relations between melilite and gehlenite is offered by the hitherto generally accepted theory of Vogt,[2] who regards both species as varying mixtures of two silicates, one the "gehlenite silicate," $R_2'''R_3''Si_2O_{10}$, and the other åkermanite, $R_4''Si_3O_{10}$. The last compound is found in slags and has recently been identified by Zambonini among the minerals of Vesuvius. In it R_4'' is principally Ca, but with a notable proportion of Mg also. A purely calcic silicate of that type has not yet been found. Vogt's theory has been seriously questioned by Bodländer and Zambonini. The new interpretation now offered seems to be more general.

The little-known mineral arctolite is possibly another member of this group, with affinities toward prehnite. Its composition is fairly expressed by the formula

$$Al_2(SiO_4)_3CaMgH_2$$

which is that of prehnite with CaMg in place of Ca_2. The integrity of this species, however, is not yet fully established.

THE FELDSPARS AND SCAPOLITES.

Although orthosilicic and trisilicic acids are technically distinct and from the chemist's point of view should be studied separately, their salts containing aluminum occur in such a variety of mixtures that in several groups of minerals the two acids must be considered as mutually equivalent and their compounds discussed together. Two such groups, closely allied, are the feldspars and the scapolites.

For each of these groups the theory developed by Tschermak has met with general acceptance. In the case of the feldspars, Tschermak

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[1] Deutsche geol. Gesell. Zeitsch., p. 237, 1892.

[2] Neues Jahrb., 1892, vol. 2, p. 73.

was undoubtedly anticipated in great part by Hunt, Waltershausen, and others, but to him full recognition is due. More recently it has been put upon a thorough quantitative basis by the synthetic experiments of Day and Allen.[1] According to this theory the triclinic plagioclase feldspars consist of albite, $AlNaSi_3O_8$, and anorthite, $CaAl_2Si_2O_8$, which, commingled in various proportions, give the intermediate oligoclase, labradorite, andesite, and so on. There are also the triclinic microcline and its monoclinic equivalent, orthoclase, both represented by the formula $AlKSi_3O_8$, the monoclinic barbierite, isomeric with albite, and the recently described carnegieite, or soda anorthite, already mentioned as an isomer of nepheline. The mineral celsian, $BaAl_2Si_2O_8$, is empirically the barium equivalent of anorthite, but it is monoclinic and isomorphous with orthoclase.[2] Hyalophane and other barium feldspars are mixtures of orthoclase and celsian.

The exact nature of the isomeric equivalencies among the feldspars is not clear; they may be due to the structure of the salts independently of the acids which they represent, or to isomerisms among the acids themselves. The latter possibility was discussed in the section on the silicic acids and seems to be the more probable, at least so far as the trisilicates are concerned, but for present purposes the problem may be left outstanding. In the discussion later of the species eudidymite and epididymite the question of isomeric trisilicates will be considered.

For the scapolite series Tschermak has elaborated a theory which is closely parallel to that of the feldspars. These tetragonal minerals are shown to be most easily interpretable as mixtures of two end compounds, meionite, $Al_6Ca_4Si_6O_{25}$, and marialite, $Al_3Na_4Si_9O_{24}Cl$. Neither end compound has yet been found in nature quite free from the other, but the variations in composition, in optical character, etc., are all accounted for, and the theory, so far as it goes, is satisfactory. I have tentatively examined some possible alternative hypotheses, and none of them fulfills all necessary conditions so well as this scheme of Tschermak's.

Upon studying the feldspars and scapolites more closely, certain analogies appear other than those indicated by the parallelism of the two series. Both groups of minerals are easily alterable, and both yield kaolin as a final product of the change. Furthermore, both alter to muscovite, or to pinite, which is only an impure pseudomorphous mica, and kaolin crystallographically has close relations with the mica family. Feldspars, scapolites, muscovite, and kaolin are therefore presumably connected, and the structural formulæ of the minerals should render the relationship apparent.

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[1] Am. Jour. Sci., 4th ser., vol. 19, p. 93, 1905.

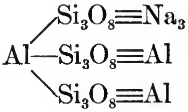
[2] Strandmark, Zeitschr. Kryst. Min., vol. 43, p. 89, 1907.

The typical empirical formulæ to be considered are now as follows:

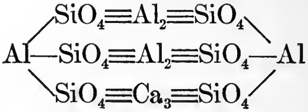
Albite	$AlNaSi_3O_8$
Anorthite	$Al_2CaSi_2O_8$
Meionite	$Al_6Ca_4Si_6O_{25}$
Marialite	$Al_3Na_4Si_9O_{24}Cl$
Muscovite	$Al_3KH_2Si_3O_{12}$
Kaolin	$Al_2H_4Si_2O_9$

For muscovite the constitution has already been indicated, and this clue, together with the general hypothesis of derivation from normal salts, enables us to correlate all six of the formulæ given. To do this it is necessary to triple the formulæ of albite and anorthite, and we have the following expressions:

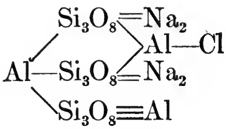
Albite.



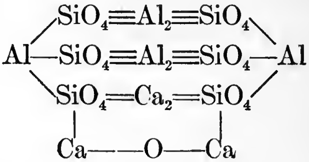
Anorthite.



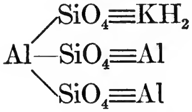
Marialite.



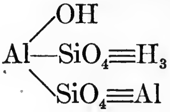
Meionite.



Muscovite.



Kaolinite.



On this basis marialite becomes the trisilicate equivalent of sodalite, although the two species are quite unlike in form. Anorthite is the calcium salt corresponding to nephelite, which is also alterable into kaolin. Again, garnets are known to alter into feldspars and scapolite, and, according to Brauns, in the alteration of diabase, prehnite and epidote are sometimes derived from anorthite. These species, therefore, are all connected by numerous cross relations, all emphasizing one another and pointing to a community of molecular type. So far the formulæ are highly suggestive, but as yet they do not indicate the mechanism of the reaction by which a trisilicate feldspar breaks down into kaolin, and they need development in that direction. Tschermak,[1] from the composition of the silicic acids derivable from the several minerals, infers that albite is a salt of the acid $H_2Si_3O_7$, and that anorthite is a basic metasilicate. Himmel-

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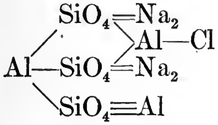
[1] Zeitschr. physikal. Chemie, vol. 53, p. 349, 1905.

bauer,[1] by the same method, makes meionite a metasilicate and marialite a derivative of a new acid, $H_{10}Si_9O_{23}$. Such formulæ fail to express the known relations of the minerals at all clearly.

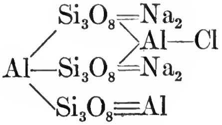
Closely allied to the feldspars in its petrographic relations is the isometric mineral leucite, $AlKSi_2O_6$. Empirically it seems to be a metasilicate and is commonly so regarded, but it may easily be conceived as a mixed salt, containing orthosilicate and trisilicate molecules. By alteration it yields orthoclase, nephelite, muscovite, and kaolin, and the pseudoleucite of Magnet Cove has been shown by J. F. Williams to consist of orthoclase and elæolite intimately commingled.[2] This case probably represents the typical breaking up of leucite, the formation of kaolin or of muscovite in other instances being due to secondary reactions. On the other hand, C. and G. Friedel[3] have obtained leucite synthetically from muscovite as a starting point, orthoclase and nephelite being produced at the same time, and Lemberg,[4] in his experiments, has transformed leucite into sanidine, anorthite, and microsommite and also into andesine. In a later paper[5] Lemberg describes the action upon various silicates of the salt $Na_2SiO_3.8H_2O$, at 200° under pressure, kaolin, albite, elæolite, leucite, and analcite all yielding a silicate-cancrinite containing SiO_3 in place of CO_3. These facts connect the several species together, but to their explanation the empirical expression $AlKSi_2O_6$ gives no clue. A formula for leucite, to be satisfactory, must be a multiple of this, and several such multiples fulfill the conditions of the problem.

The isometric form of leucite suggests at once a relation with the sodalite group, and this can be indicated by the quadrupled formula $Al_4K_4Si_8O_{24}$. We then have, as a distinct possibility, the following series of molecules, including for comparison the tetragonal marialite.

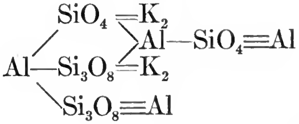
Sodalite.



Marialite.



Leucite.



On this basis leucite is clearly reduced to the uniform type of the minerals to which it is apparently related, and also of those into which it alters, but the formula proposed can not be regarded as final. It is offered here only as a first approximation toward answering the questions which are suggested and is therefore subject to modification in the future.

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[1] Sitzungsber. K. Akad. Wiss. Wien., vol. 119, p. 115, 1910.

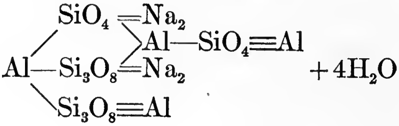
[2] Arkansas Geol. Survey Ann. Rept., 1890, vol. 2, pp. 267 et seq.

[3] Soc. min. Bull., vol. 13, p. 134, 1890.

[4] Deutsche geol. Gesell. Zeitschr., 1876, pp. 611-615.

[5] Idem, 1885, pp. 961, 962.

Closely allied to leucite is another isometric mineral, analcite, which empirically has the composition $AlNaSi_2O_6.H_2O$. This species alters, like leucite, into feldspar, and an alteration into prehnite is also recorded. Furthermore, Lemberg has shown, in the papers already cited, that leucite, by the action of soda solutions, may be transformed into analcite, and that analcite, by similar treatment with potash, yields leucite again. With these facts in view, analcite may be written exactly equivalent to leucite. That the water is entirely nonconstitutional has been shown by the experiments of G. Friedel,[1] who found that it could be expelled continuously without change in the crystal nucleus. The dehydrated mineral, moreover, could take up water again, or instead of water various vapors and gases. These substances seem to be occluded, much as water is held in a sponge, only the ratio between the water and the silicate is definitely molecular. This phenomenon seems to be peculiarly characteristic of the zeolites, which will be considered in the next section of this bulletin.



The close relationship between leucite and analcite is shown not only by the work of Lemberg but also by investigations carried out in the laboratory of the Geological Survey by Clarke and Steiger.[2] When these minerals are heated with dry ammonium chloride in sealed tubes to 350° C., double decomposition takes place and ammonium is substituted for the fixed alkalies. In each case the new compound has the empirical formula $NH_4AlSi_2O_6$; that is, an ammonium analcite or leucite precisely equivalent to the original silicates is formed. A volatile base has replaced the fixed bases, and the substance so formed splits up on ignition in such a way as to shed light on its constitution. If, now, ammonium leucite is a true metasilicate, a salt of the acid H_2SiO_3, it should break up, when ignited, in accordance with the following equation:

$$2\ NH_4Al(SiO_3)_2 = Al_2(SiO_3)_3 + 2\ NH_3 + H_2O + SiO_2$$

and one-fourth of the silica ought to be set free, measurable by extraction with sodium carbonate solution. No such liberation of silica occurs, and we may therefore conclude that analcite and leucite are not metasilicates, but more probably mixed orthosilicates and trisilicates, as shown in the constitutional formulæ assigned to them here. The evidence against their being metasilicates at least seems to be conclusive.

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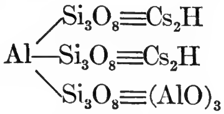
[1] Soc. min. Bull., vol. 19, pp. 94, 363, 1896.

[2] U. S. Geol. Survey Bull. 207, 1902.

One other isometric mineral, pollucite, may perhaps be considered here. Its empirical formula, as established by the analyses of Wells[1] and Foote,[2] is that of a metasilicate, $H_2Cs_4Al_4S_9O_{27}$, which, however, may also be written as a basic trisilicate, thus:



$$\mathrm{Al}\begin{array}{l}\diagup \mathrm{Si_3O_8{\equiv}Cs_2H}\\ —\mathrm{Si_3O_8{\equiv}Cs_2H}\\ \diagdown \mathrm{Si_3O_8{\equiv}(AlO)_3}\end{array}$$

If further investigations should show that the water of pollucite is not an essential part of the molecule, its empirical formula would be very close to $AlCsSi_2O_6$, and the mineral would become the cæsium equivalent of leucite and analcite. Pollucite, however, differs from those minerals in one notable respect, namely, on heating with dry ammonium chloride only one-third of its cæsium is replaced by ammonium instead of the entire amount. This observation needs to be checked by experiments on pollucite from new localities before any safe conclusions can be drawn from it. That pollucite is a true metasilicate is very doubtful.

Although kaolin mineralogically is not a member of the feldspar group, it is properly discussible here as a derivative. The formula assigned to it in the foregoing pages is not unimpeachable, but it suggests its relations to the feldspars and micas and also represents the fact that the water in it is wholly constitutional. In fact the mineral is stable far above the ordinary temperatures of dehydration, so that the water can be regarded only as an essential part of the molecule.

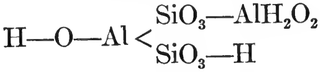
In addition to the formula proposed for kaolin the following expressions are possible without assumption of any higher molecular weight:

(1) $Si_2O_7.H_4(AlO)_2$

(2) $Si_2O_7.H_2(AlOH)_2$ (Brauns's)

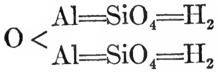
(3) $Si_2O_5.(AlH_2O_2)_2$ (Groth's)

(4)



$$\mathrm{H{—}O{—}Al} < \begin{array}{l}\mathrm{SiO_3{—}AlH_2O_2}\\ \mathrm{SiO_3{—}H}\end{array}$$

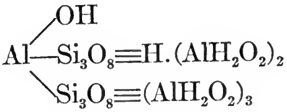
(5)



$$\mathrm{O} < \begin{array}{l}\mathrm{Al{=}SiO_4{=}H_2}\\ \mathrm{Al{=}SiO_4{=}H_2}\end{array}$$

If the formula be tripled, then kaolin may be written as a basic trisilicate, thus:

(6)



$$\mathrm{Al}\begin{array}{l}\diagup \mathrm{OH}\\ —\mathrm{Si_3O_8{\equiv}H.(AlH_2O_2)_2}\\ \diagdown \mathrm{Si_3O_8{\equiv}(AlH_2O_2)_3}\end{array}$$

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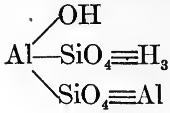
[1] Am. Jour. Sci., 3d ser., vol. 41, p. 213, 1891.

[2] Idem, 4th ser., vol. 1, p. 457, 1896.

Of all these symbols only the last and the one originally chosen indicate the relations between kaolin and its parent species. As for these two, the formula



$$\mathrm{Al}\begin{cases}\mathrm{OH}\\ \mathrm{SiO_4\equiv H_3}\\ \mathrm{SiO_4\equiv Al}\end{cases}$$

is the simpler and would seem to represent the greater stability. Kaolin under ordinary circumstances is scarcely attacked by the strongest hydrochloric acid, a fact which seems to be most in harmony with the orthosilicate expression. That expression, therefore, is to be preferred, at least until more positive evidence is attainable. It is also sustained by the observation of Cornu[1] that kaolin has a faintly acid reaction toward litmus. The three hydrogen atoms in union with the SiO_4 group suggest such an acidity.

After dehydration at low redness, kaolin is completely decomposable by hydrochloric acid, but the ignited mass contains no silica soluble in sodium carbonate solution. These facts, developed by experiments made under my direction by Mr. George Steiger, seem to indicate the formation of a salt, $Al_2Si_2O_7$, as the result of ignition, but other interpretations are possible. The data are given here simply as data that may become available for a fuller discussion of the problem by and by. It will be seen later, when the other clays are considered, that their formulæ are in harmony with that chosen for kaolin.

THE ZEOLITES.

By this title is indicated a well-defined group of hydrous silicates, unmistakably related to nephelite and the feldspars. Indeed the relationship is so close that the several species can often be studied genetically, and it has also been established in certain cases by synthetic methods. The kinship of analcite, which is commonly classed as a zeolite, to nephelite and leucite, has already been pointed out.

For example, hydronephelite, natrolite, and analcite all occur as alteration products of nephelite;[2] natrolite and analcite are both derivable by natural processes from albite,[3] and analcite yields feldspathic pseudomorphs. Natrolite and hydronephelite may be generated from sodalite, and by artificial means Doelter[4] has produced natrolite and analcite from nephelite. All these relations, with others both morphologic and genetic, are covered by the types of formulæ which have already been developed and which can be extended here.

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[1] Min. pet. Mitt., vol. 24, p. 417, 1905; idem, vol. 25, p. 489, 1906.

[2] See Brögger, Zeitschr. Kryst. Min., vol. 16, pp. 223 et seq., 1890.

[3] See Brauns, Neues Jahrb., 1892, vol. 2, p. 1.

[4] Neues Jahrb., 1890, vol. 1, p. 134.

In a similar way, but rather less completely, many zeolitic minerals may be connected with anorthite, the calcium end of the plagioclase feldspar series. For example, by heating anorthite with freshly precipitated silica and carbonic acid water at 200°, Doelter obtained heulandite.[1] Furthermore, by various wet reactions, some of them unfortunately involving several stages, Lemberg[2] has generated analcite from chabazite, gmelinite, laumontite, harmotome, phillipsite, stilbite, and heulandite, for some of these minerals studying several varieties of one species. It is clear, therefore, that the zeolites are connected not only with the feldspars but also with one another by many interlacing relations which their constitutional formulæ ought to symbolize. These relations have been recognized by all modern authorities, but their interpretations have been diverse.

In the systematic treatment of the zeolites the most serious difficulty is found in the hydration of the several species. To determine what part of the water in any one of these minerals is constitutional and what is crystalline is not easy, and no fixed criterion exists upon which judgment may be based. At present the weight of evidence goes to show that zeolitic water is extraneous to the silicate molecule, at least so far as suitable experiments have been made. But until all zeolites have been studied by modern methods it would be unwise to assume that the rule is universal. Indeed, in some zeolites it seems probable that constitutional water or hydroxyl is actually present, for on no other basis are the analyses easily interpretable. The work of Friedel on analcite, a mineral in which the water is clearly extraneous, was cited in the preceding section of this chapter, and analogous researches have been conducted by other investigators.[3] Many zeolites lose water, which is regained without much change of crystalline character on subsequent exposure of the minerals to moist air, and this water at least can not be regarded as constitutional. The fundamental fact, however, that zeolitic water is held in relatively simple molecular ratios must not be overlooked, even though it may not be clearly explainable. It is also to be remembered that the hydrated silicates differ in crystalline form from the parent anhydrous minerals.

In the former edition of this memoir[4] an attempt was made to discriminate between essential and nonessential water in the zeolites, on the basis of various researches (Damour, Hersch, and others) relative to their dehydration at successive temperatures. The results obtained were instructive and of some significance, but the modern

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[1] Neues Jahrb., 1890, vol. 1, p. 128 et seq.

[2] Deutsche geol. Gesell. Zeitschr., 1885, p. 959 et seq.

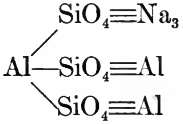
[3] See Rinne (Neues Jahrb., 1896, vol. 1, p. 139; idem, 1897, vol. 1, p. 41), on heulandite and stilbite, and Grandjean (Soc. min. Bull., vol. 33, p. 5, 1910) on the replacement of zeolitic water by other gases and vapors. Zambonini (Contributo allo studio dei silicati idrati, 1908) has also done much to show that zeolitic water is essentially absorptive.

[4] U. S. Geol. Survey Bull. 125, 1895.

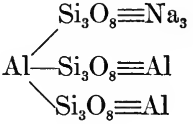
work, as just cited, renders a complete revision of the subject necessary. Now, regarding water as not belonging to the true silicate molecules, we may discuss the zeolites with reference to their genetic relations, beginning with the obviously related starting points, the formulæ of nephelite and albite. These minerals, as we have already seen, are compounds of the same type, one an orthosilicate, the other a trisilicate, $Al_3(SiO_4)_3Na_3$ and $Al_3(Si_3O_8)_3Na_3$. From these species hydronephelite, natrolite, scolecite, mesolite, analcite, and faujasite appear to be derived, either directly or indirectly, as the formulæ to be proposed clearly show. In nearly every case the simplest empirical formula is discarded as not fairly representing the known relations between the minerals, and to only one of the above-named species does the rule not apply. That species is hydronephelite,[1] an obvious derivative of its original type and of its more direct parent, sodalite. Its formula is $Al_3(SiO_4)_3Na_2H.3H_2O$.

For natrolite alternative formulæ have been proposed. One, $Al_2(SiO_4)_3Na_2H_4$, regards the water of the mineral as constitutional. But when natrolite is heated with dry ammonium chloride in a sealed tube it is transformed into the compound $Al_2(NH_4)_2Si_3O_{10}$, an orthotrisilicate. The simplest formula for natrolite, then, is $Al_2Na_2Si_3O_{10}.2H_2O$, which is not obviously related to nephelite or to its near relatives among the zeolites. Nephelite can be written as a basic orthotrisilicate, but that involves more difficulties than the one it might seek to avoid. Natrolite, then, with other species, is best represented in a less immediately obvious manner by doubling its formula and bringing it into line with its congeners, especially with sodalite, scolecite, mesolite, and edingtonite. Mesolite, however, is only a crystalline mixture of natrolite and scolecite and needs little consideration. Edingtonite is rather doubtful, but Lemberg,[2] by the action of barium chloride solution upon natrolite, obtained a silicate which appears to be that mineral. This species is included here on account of its chemical analogy to scolecite. So much premised, the formulæ now offered are as follows, beginning with the anhydrous type species:

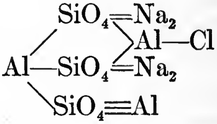
Nephelite.



Albite.



Sodalite.



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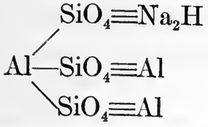
[1] Thugutt (Neues Jahrb., 1910, vol. 1, p. 25) regards hydronephelite as a mixture of natrolite, gibbsite, and diaspore; but the mineral analyzed by me was purified by means of Thoulet solution, was homogeneous under the microscope, and apparently hexagonal as judged from its optical behavior.

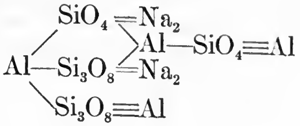
[2] Deutsche geol. Gesell. Zeitschr., vol. 28, p. 553, 1876.

Hydronephelite.



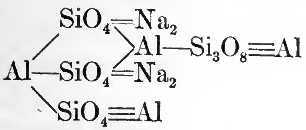
$3H_2O$

Analcite.



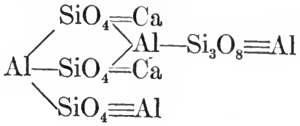
$4H_2O$

Natrolite.



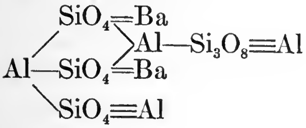
$4H_2O$

Scolecite.



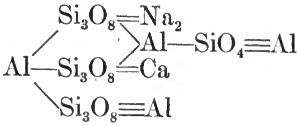
$6H_2O$

Edingtonite.



$6H_2O$

Faujasite.



$19H_2O$

The formula assigned to faujasite is quite unlike that usually given, but it best fits Damour's analysis, as the subjoined comparison shows:

	Found.	Calculated.
SiO_2	46.12	47.46
Al_2O_3	16.81	16.14
CaO	4.79	4.43
Na_2O	5.09	4.91
H_2O	27.02	27.06
	99.83	100.00

The isometric character of faujasite relates it to analcite and leucite, but its immediate derivation was probably from albite.

A group of monoclinic zeolites, closely related in structure to the foregoing species, is that formed by wellsite, phillipsite, harmotome, and stilbite, to which Pratt and Foote[1] assign the following generalized formulæ:

Wellsite	$RAl_2Si_3O_{10}.3H_2O$
Phillipsite	$RAl_2Si_4O_{12}.4H_2O$
Harmotome	$RAl_2Si_5O_{14}.5H_2O$
Stilbite	$RAl_2Si_6O_{16}.6H_2O$

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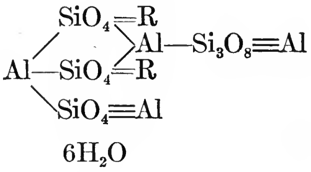
[1] Am. Jour. Sci., 4th ser., vol. 3, p. 443, 1897.

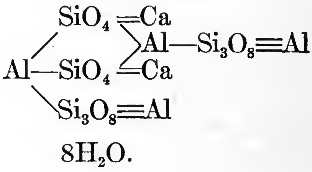
These formulæ make a beautifully regular series, but unfortunately they do not represent the wide variations in composition exhibited by some of the species. Harmotome, a barium salt, and stilbite, a calcium compound, are fairly constant, except for variable replacements of the dyad radicle by sodium or potassium. Wellsite rests on a single analysis, in which calcium, barium, strontium, potassium, and sodium appear. In phillipsite R is principally calcium, but with varying replacements by potassium and sodium, and the ratio of silicon to oxygen is by no means constant. A phillipsite reported by Zambonini[1] is very near $R''Al_2Si_3O_{10}.4H_2O$, with alkalies partly replacing lime. Other phillipsites are much richer in silica and approach a trisilicate in composition. In fact, all phillipsites appear to be mixtures of orthosilicates and trisilicates, ranging between $3Si_3O_8 : 1SiO_4$, and $1Si_3O_8 : 3SiO_4$. Such a range and even a greater one is only to be expected when we remember that many zeolites are derivatives of plagioclase feldspars. The zeolites vary as the feldspars vary between end products, which may or may not be definitely known. Stilbite, for instance, represents a hydrated calcium albite or trisilicic anorthite, which in the anhydrous condition is yet to be discovered.

In this series of silicates, then, we have the plagioclase variation in the ratio Si : O, whereas the ratios R : Al and the degree of hydration for each species are constant or nearly so. The formulæ being qualified by recognizing the common replacements of lime or barium by alkalies, the four "species" may be assigned the following general expressions, that for phillipsite representing a fair average between its extreme variations:

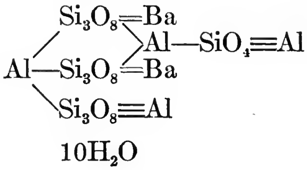
Wellsite.



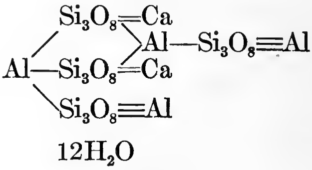
Phillipsite.



Harmotome.



Stilbite.



In phillipsite as much as half the calcium may be replaced by potassium. That replacement is characteristic of the species.

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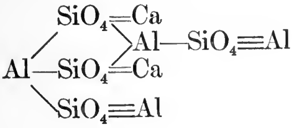
[1] Contributo allo studio dei silicati idrati, p. 114, 1908.

The hydration of these silicates increases in a very regular and remarkable manner, and proportionally to the number of silicon atoms in the molecule. For every silicon atom one molecule of water is retained. This rule holds true for the typical formulæ, but if individual analyses are studied considerable variations will be found. Phillipsite nearly always contains an excess of water. Moreover, the low molecular weight of water is the cause of apparent irregularities when formulæ are deduced from analytical data. A small error in the determination of water is exaggerated in the computed ratios. The rule is not universal, but it certainly applies to the wellsite-stilbite series. Stilbite, at one end, is entirely trisilicate; at the other end there should be a pure orthosilicate $R_2Al_4(SiO_4)_4.4H_2O$, but no such zeolite is known. The orthorhombic thomsonite approaches the required composition but not quite closely enough. Empirically either lawsonite or its isomer hibschite would complete the series, but their hydration appears to be constitutional, and crystallographically they belong elsewhere.

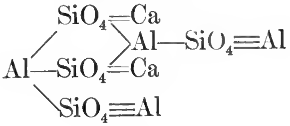
Among the plagioclase zeolites, if such a term is admissible, there are two, essentially orthosilicates, which may be regarded as hydrated anorthite. These species are thomsonite and gismondite, and they may be represented as anorthite plus water, using the tripled formula for anorthite as developed in the preceding section of this work. It is better perhaps to treat them as less condensed molecularly than anorthite, because of the loose crystalline structure which permits the retention of zeolitic water. On this basis their formulæ fall in line with those of the other zeolites, as follows:

Thomsonite.



$5H_2O$

Gismondite.[1]



$8H_2O$

In each of these minerals variations are common, just as among the feldspars from which they are probably derived. Gismondite contains some potassium replacing calcium, or, in other words, an admixture from orthoclase or microcline. Thomsonite may have as much as half its lime replaced by soda, due perhaps to original carnegieite, and it often carries an excess of silica, either in "solid solution" or else representing trisilicate groups. Carnegieite, it should be remembered, is an isomer of nephelite, a species that, under some conditions, alters into thomsonite.

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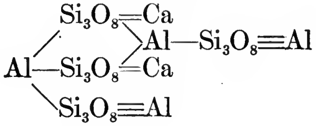
[1] See Zambonini (Neues Jahrb., 1902, vol. 2, p. 79) for the composition of gismondite and also of phillipsite. See also Sachs, Centralbl. Mineralogie, 1904, p. 215.

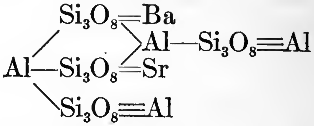
Three more zeolites, like stilbite, are entirely trisilicate, namely, heulandite, epistilbite, and brewsterite. Heulandite and epistilbite are isomeric, or in crystallographic terminology the compound is dimorphous. They differ from stilbite in containing less water, 11 molecules instead of 12. The formula commonly assigned to them, if doubled as is done here, assumes only 10 molecules of water, but all trustworthy analyses give a larger proportion. Brewsterite differs from them in its dyad bases, having barium and strontium with only a little lime. In the formula to follow presently the calcium is united with barium. In heulandite strontium is often present, and soda to a small extent replaces lime. The two formulæ, identical in type with those which have preceded them, are as follows:

Heulandite.



$11H_2O$

Brewsterite.

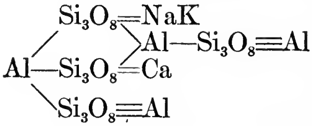


$10H_2O$

Brewsterite evidently is derived from an unknown feldspar containing strontium. Edingtonite and harmotome may represent original celsian or hyalophane. Doelter's synthesis of heulandite from anorthite has already been mentioned, but an interesting observation by Rinne[1] remains to be noticed. On decomposing heulandite with sulphuric acid he obtained a crystalline form of silica, which appeared to be cristobalite. This fact may shed some light on the relative molecular magnitude of the zeolite, as was suggested in Chapter II, on the silicic acids.

Baschieri,[2] working by Tschermak's method, regards heulandite and stilbite as salts of an acid, $H_{10}Si_6O_{17}$. Natrolite and laumontite yielded him orthosilicic acid, and analcite he formulates as a dimetasilicate.

Erionite, an orthorhombic zeolite described by Eakle,[3] probably belongs as a trisilicate with stilbite and heulandite. Its formula, which accurately reflects Eakle's analysis, is as follows:



$12H_2O$

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[1] Neues Jahrb., 1896, vol. 1, p. 139.

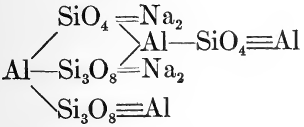
[2] Zeitschr. Kryst. Min., vol. 46, p. 479, 1909.

[3] Am. Jour. Sci., 4th ser., vol. 6, p. 66, 1898.

Laumontite, chabazite, gmelinite, and levynite are plagioclase zeolites in which the ratios are empirically metasilicate or nearly so. That is, SiO_4 and Si_3O_8 groups appear in equal or approximately equal numbers. Laumontite is essentially calcic, with insignificant alkaline replacements. In gmelinite alkalies predominate and lime is quite subordinate. Chabazite varies widely from a calcic variety to one which is mainly alkaline, and levynite is a lime zeolite with SiO_4 to Si_3O_8 as 3 to 2. The variations in composition are quite like those which occur among the feldspars, and the crystalline comminglings are of the same order. If regarded as a zeolite, analcite is of similar constitution to these species but of lower hydration and less variability.[1] Lemberg's syntheses of analcite from three of them have already been mentioned.

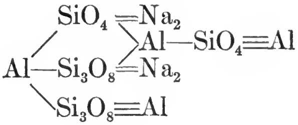
Now, repeating the formula of analcite to facilitate comparison, the several zeolites can be well represented as follows:

Analcite.



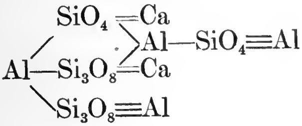
$4H_2O$

Gmelinite.



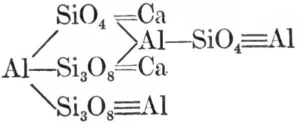
$12H_2O$

Laumontite.



$8H_2O$

Calcium chabazite.



$12H_2O$

Sodium chabazite is empirically identical with gmelinite but different in form. This silicate therefore appears to be dimorphous or isomeric, and the possibility of isomerism is easily shown. One acid radicle is represented in what may be called the side chain of the molecule as SiO_4. Let that exchange places with an Si_3O_8 group and an isomeric arrangement is at once given. There are other possibilities, but the one is enough for present purposes. As for the last of these plagioclase zeolites, levynite, the best analyses represent a mixture of three orthosilicate and two trisilicate molecules of the same type as the other members of the group, with calcium for the dyad radicle, and 10 molecules of water. The formula commonly assigned to levynite, $CaAl_2Si_3O_{10}.5H_2O$, does not fit the facts. From Hillebrand's analysis of the Table Mountain levynite we get the following comparison between observation and theory:

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[1] On variations in the composition of analcite see Foote and Bradley, Am. Jour. Sci., 4th ser., vol. 33, p. 433, 1912.

	Found.	Calculated.
SiO_2	46.76	46.55
Al_2O_3	21.91	21.98
CaO	11.12	12.07
Na_2O	1.34	
K_2O	.21	
H_2O	18.65	19.40
	99.99	100.00

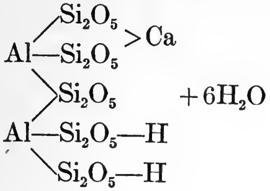
So far all the zeolites considered, except hydronephelite, are assigned one type of formula with varying hydration. If we unite SiO_4 and Si_3O_8 under the indiscriminate symbol X, the general formula becomes

$$(R'',R'_2)_2Al_4X_4.nH_2O$$

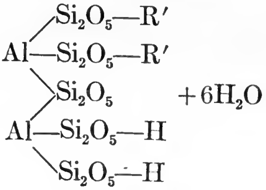
and this covers all variations of composition accurately. R″ may stand for calcium, strontium, or barium, and R′ for either sodium or potassium. The derivation of the zeolites from feldspar and lenads, however, is not always direct. In many cases it can be observed and verified, but in others the zeolites seem to have been formed in cooling magmas from feldspathic material rather than from the feldspars themselves. Inclosed bubbles of water, perhaps magmatic water, have helped to generate the zeolites, especially in amygdaloid rocks. The zeolitic amygdules can hardly be explained otherwise, and in such a process the SiO_4 and Si_3O_8 radicles may easily be supposed to change places, forming the silicate nuclei corresponding to calcium albite on the one hand and sodium anorthite or carnegieite on the other.

Regardless of the validity on nonvalidity of the foregoing suggestions, which, by the way, are not new, the constitutional and genetic connection between the normal zeolites and the feldspars seems to be perfectly clear, and it ought to be easily confirmed by petrographic investigation. Data of this kind, in addition to those already cited, are even now available, and many alterations of the most pertinent kind have been observed. Thus laumontite, heulandite, stilbite, and analcite alter into albite or orthoclase; laumontite and stilbite into analcite; chabazite into natrolite; and gismondite into phillipsite. So also alterations into prehnite are recorded on the part of laumontite, scolecite, mesolite, natrolite, and analcite, and the identity of chemical type seems to be almost unquestionable. From the formulæ here developed all these alterations become intelligible, and the theory of substitution from normal salts is very emphatically sustained.

Several other zeolitic minerals are known, which, however, do not belong in the normal series. The two closely allied species mordenite and ptilolite, for example, are to be classed as metadisilicates, and their constitution, which I have fully discussed elsewhere,[1] is easily expressed by regarding both minerals as mixtures of the two molecules

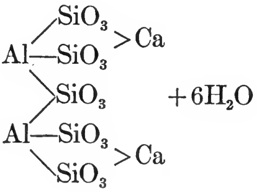


and



in which R′ = Na or K. In one occurrence of ptilolite the water is lower than is required by these formulæ, and it seems probable that a trihydrate may exist.

The metasilicate zeolite, laubanite, is the precise equivalent of ptilolite and mordenite and is easily interpreted thus:

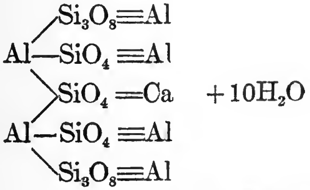


Pilinite, a similar mineral, seems to be $Al_2(SiO_3)_5Ca_2.H_2O$, a monohydrate corresponding to the hexhydrated laubanite. Unlike laubanite, pilinite is undecomposed by hydrochloric acid, but physically all four of the species here grouped together resemble one another very closely.

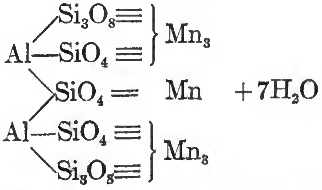
Possibly bavenite,[2] $Ca_3Al_2Si_6O_{18}.H_2O$, is to be classed with laubanite as a metasilicate, although different in structure.

Foresite and the manganese zeolite ganophyllite are two more species of unusual form. Their formulæ can be written thus:

Foresite.



Ganophyllite.



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[1] Am. Jour. Sci., 3d ser., vol. 44, p. 101, 1892.

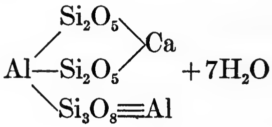
[2] See Artini, R. accad. Lincei Atti rendiconti, vol. 10, p. 139, 1901.

These expressions represent fairly well the actual composition of the two minerals, the analysis of foresite by Manasse[1] and that of ganophyllite by Hamberg[2] being taken for comparison.

	Foresite.		Ganophyllite.	
	Found.	Calculated.	Found.	Calculated.
SiO_2	48.93	49.91	39.67	42.69
Al_2O_3	27.56	28.28	7.95	8.60
Fe_2O_3			.90	
CaO	5.16	5.18	1.11	39.29
MgO			.20	
MnO			35.15	
Na_2O	1.14		2.18	
K_2O			2.70	
PbO?			.20	
H_2O	16.66	16.63	9.79	9.96
	99.45	100.00	99.85	100.00

Both species need additional study, especially with reference to their possible variations.

A still more unusual type of zeolite is stellerite, recently described by Morozewicz.[3] To this the empirical formula $CaAl_2Si_7O_{18}.7H_2O$ is assigned, which constitutionally is equivalent to



Grattarola's pseudonatrolite seems to have nearly the same formula, but with only $5H_2O$. The structure proposed for these species is, of course, only tentative, and may be set aside at some future time.

A considerable number of other zeolitic minerals have been described, but their nature is by no means clear. Offretite may be a variety of phillipsite, unusually rich in potash, and gonnardite may belong with natrolite and scolecite. References to other imperfectly known zeolites may be found in Dana's Mineralogy.

The morphological characteristics of the zeolites probably depend in great part upon their mode of hydration, but this point needs to be developed. So also does the relation between zeolites and kaolin, into which the minerals of this group sometimes alter. Furthermore, zeolitic substances of indeterminate nature are believed to exist in soils and clays, and it is conceivable that such bodies may be intermediately formed during the transition from feldspar into kaolin. In

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[1] Zeitschr. Kryst. Min., vol. 35, p. 514, 1902.

[2] Geol. Fören. Förh., vol. 12, p. 586, 1891.

[3] Acad. Cracovie Bull., 1909, vol. 2, p. 344.

studying the mechanism of that change this possibility ought to be considered.

THE MICAS AND CHLORITES.

On account of their wide distribution, their variety of composition, and their genetic relations to other species, the micas and chlorites form one of the most instructive and interesting families of minerals. Two of the micas, muscovite and biotite, have already been noted among the members of the first and second of the preceding groups; and we have seen how frequently they are produced by the alteration of other silicates, some of which have been synthetically derived from micaceous material.

As regards the substitution theory, the minerals of this family are peculiarly suggestive, for the reason that they form a series of the most complete character. Thus, starting from the normal aluminum orthosilicate, we have

Normal orthosilicate	$Al_4(SiO_4)_3$
Muscovite	$Al_3(SiO_4)_3KH_2$
Normal biotite	$Al_2(SiO_4)_3Mg_2KH$
Normal phlogopite	$Al(SiO_4)_3Mg_3KH_2$

No further substitution of the same order is possible, for the reason that it would remove the linking atom of aluminum, and break up the fundamental molecule.

Muscovite, the first species in the foregoing series, occurs in nature as an independent mineral, and also as an alteration product of nephelite, eucryptite, topaz, andalusite, the feldspars, the scapolites, and various other natural silicates. All these alterations become intelligible in the light of the formulæ adopted in this memoir. In its more typical occurrences muscovite agrees sharply with the formula given, but it varies in composition within well-defined limits. First, it ranges toward its sodium equivalent, paragonite, which has the corresponding formula $Al_3(SiO_4)_3NaH_2$. Secondly, in fuchsite, the chromic mica, a chromium salt partly replaces the aluminum compound, and similar ferric replacements are also known. The chromic replacement is generally quite small, and so, too, is that of iron, although one sericite (a secondary muscovite), analyzed by Sennhofer,[1] is very nearly represented by $Al_2Fe(SiO_4)_3KH_2$. Much larger replacements of aluminum by vanadium are found in the mineral roscoelite, in which as much as 24 per cent of V_2O_3 has been determined. An ideal roscoelite should have the formula $AlV_2(SiO_4)_3KH_2$, requiring 33.6 per cent of V_2O_3, but the pure compound is yet to be discovered. In kryptotile, $Al_3(SiO_4)_3H_3$, we have probably the extreme hydrogen end of the muscovite series, and leverrierite may be the same species but of different origin. The presence of

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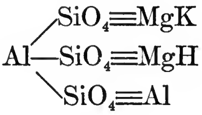
[1] Min. pet. Mitt., vol. 5, p. 188, 1882–83; Dana, E. S., System of mineralogy, 6th ed., table, p. 618, 1892, analysis No. 43.

magnesia or of ferrous iron in a muscovite is attributable to small admixtures of biotitic molecules.

The most important variation in muscovite is in the direction of increased silica. Normal muscovite contains 45.3 per cent of SiO_2, but varieties exist in which the percentage rises to nearly 59. Muscovites of this class have been designated by Tschermak as phengites, and they are most easily explained upon the supposition of trisilicate admixtures. The molecule $Al_3(Si_3O_8)_3KH_2$ is identical in type with ordinary orthosilicate muscovite, and its presence completely accounts for all excesses of silica over the normal amount. In Sandberger's lepidomorphite, for instance, the orthosilicate and trisilicate molecules occur in nearly equal proportions. All known muscovite may be represented by the general formula $Al_3(SiO_4)_3R'_3+Al_3(Si_3O_8)_3R'_3$, in which the latter molecule varies from 0 to 50 per cent, and with ferric iron, chromium, or vanadium sometimes partly replacing aluminum. The authenticity of this trisilicic variation is fully confirmed by certain of the lithia micas, in which the ratios are entirely trisilicate. Allied to muscovite and paragonite there is also the basic mica euphyllite, in which the univalent group $—Al{=}(OH)_2$ appears. The formula of euphyllite appears to be $Al_3(SiO_4)_3KH(AlO_2H_2)$, which agrees closely with the best analyses.

With the biotites and phlogopites the variability of composition is much greater than in the muscovite series. Typical or normal biotites may be represented by the subjoined formulæ, the actual minerals, however, being commonly mixtures.

1



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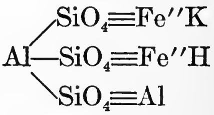

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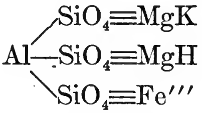

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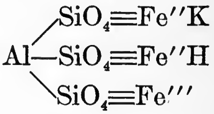


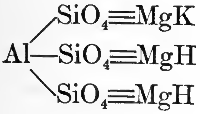
These formulæ correspond to the following compositions:

	1	2	3	4
SiO_2	43.06	37.35	40.27	35.22
Al_2O_3	24.40	21.16	11.41	9.98
Fe_2O_3			17.89	15.66
MgO	19.14		17.89	
FeO		29.88		28.18
K_2O	11.25	9.75	10.52	9.20
H_2O	2.15	1.86	2.02	1.76
	100.00	100.00	100.00	100.00

The siderophyllite of Lewis agrees very closely with No. 2 of these formulæ. Haughtonite is near an equimolecular mixture of Nos. 1 and 2, with some ferric replacement of aluminum. Sodium, as in muscovite, often partly replaces potassium.

In the normal phlogopite series four typical compounds may occur, but the entirely magnesian variety is the only one which is found even approximately pure. These compounds are—

5



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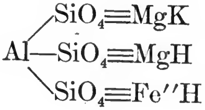

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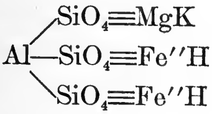

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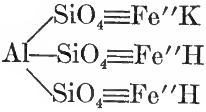

equivalent to the following percentage compositions:

	5	6	7	8
SiO_2	43.27	40.18	37.66	35.16
Al_2O_3	12.26	11.38	10.67	9.96
MgO	28.85	17.86	8.37	....
FeO	....	16.07	29.70	42.19
K_2O	11.29	10.49	9.83	9.18
H_2O	4.33	4.02	3.77	3.51
	100.00	100.00	100.00	100.00

A sodium phlogopite containing no potassium has been described by Grünling,[1] but his analysis is not altogether satisfactory. Aspidolite is another mineral which is probably sodium phlogopite, but it needs reexamination. In manganophyll, a manganese mica of variable composition, with from 9.7 to 17.1 per cent of MnO, the molecule $Al(SiO_4)_3Mn_3KH_2$ seems to occur. It is intimately associated with the manganese zeolite, ganophyllite, which is itself micaceous in appearance. The two minerals are closely related.

To the typical biotite and phlogopite molecules few natural micas actually correspond, although intermediate mixtures are very common. Many of the analyses, moreover, are difficult to interpret with any degree of accuracy and for several reasons. The state of oxidation of the iron is frequently uncertain, because in grinding a mineral for analysis ferrous compounds may be partly oxidized to the ferric condition. In fine grinding, furthermore, some water is adsorbed

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[1] Zeitschr. Kryst. Min., vol. 33, p. 218, 1910.

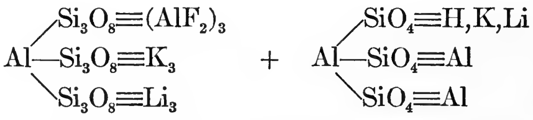
from the atmosphere, and an error by no means small is thereby incurred. Titanium is also present in many micas, and its exact function in them is quite unknown. It may be present as TiO_2 replacing silica, as Ti_2O_3 replacing alumina, or, which is probably more common, as inclusions of rutile. An unusual type of mica is Breithaupt's alurgite, which, as analyzed by Penfield,[1] corresponds to a mixture of molecules—

$$\begin{gathered} 2Al_3(Si_3O_8)_3KH_2 \\ 3Al_2(SiO_4)_3K_2H_4 \\ 3Al_2(SiO_4)_3Mg_2KH \end{gathered}$$

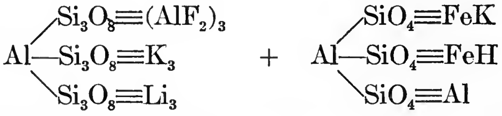
with a slight excess of H over K in the last compound. The second of these molecules, an alkaline biotite, is the characteristic feature of alurgite. Similar compounds, parallel to phlogopite, seem also to exist, having the general formula $Al(SiO_4)_3R'_9$, but all of these bodies conform sharply to the general theory of the micas and are substitution derivatives of the normal aluminum salt.

In many of the magnesian micas fluorine is found, and the iron micas frequently contain oxygen in excess of the amount necessary to convert all the silicon into the radicle SiO_4. When this excess is real, that is, not ascribable to defective analysis, it may be due either to alteration or to the replacement of univalent radicles by such groups as AlO_2H_2, and $R''OH$. Replacements of this kind indicate a transition toward the chlorites, as will be seen later.

Fluorine in the ferromagnesian micas may represent either a group like $—Al{=}F_2$ or $—R''—F$, and these appear most conspicuously in the lithia micas. An average lepidolite, for example, agrees well with the formula



That is, the mineral is a mixture of a trisilicate with a muscovite, the actual proportions varying on both sides of the ratio 1 : 1. Lepidolite sometimes forms borders on plates of muscovite, and Baumhauer[2] has shown that lepidolite often contains inclusions of muscovite recognizable only under the microscope. Another lithia mica, zinnwaldite, is a similar mixture of the same trisilicate with a ferrous biotite, thus:



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[1] Am. Jour. Sci., 3d ser., vol. 46, p. 289, 1893. Penfield's interpretation of alurgite is quite different from that adopted here.

[2] Zeitschr. Kryst. Min., vol. 51, p. 344, 1913.

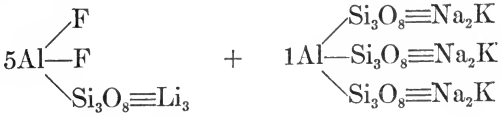
which represents its composition very closely. The calculated composition of the two micas is as follows:

	Lepidolite.	Zinnwaldite.
SiO_2	51.43	46.54
Al_2O_3	25.50	21.58
FeO	....	10.15
K_2O	13.43	13.27
Li_2O	4.29	3.17
H_2O	.64	.63
F	8.13	8.04
	103.42	103.38
Less O	3.42	3.38
	100.00	100.00

In both minerals a little potassium is commonly replaced by sodium, and a little fluorine by hydroxyl. Cryophyllite is near zinnwaldite but more complicated. It forms borders on plates of the iron mica annite, which is a mixed silicate between a biotite and a phlogopite, and its derived lithia mica exhibits similar complexity. Other known lithia micas are varying mixtures of the typical molecules found among the other members of this group of minerals, and in irvingite, which is fully two-thirds trisilicate, an alkaline biotite appears. Irvingite is well represented by the formula

$$8Al(Si_3O_8)_3(AlF_2)_3K_3Li_3+9Al_2(Si_3O_8)_3K_2H_4+11Al_2(SiO_4)_3Li_3Na_3.$$

Polylithionite, which is entirely a trisilicate mica, has a quite different type of formula from those already given. The typical mineral as shown by Lorenzen's analysis has the formula



$$5Al\begin{cases}F\\ F\\ Si_3O_8{\equiv}Li_3\end{cases} + 1Al\begin{cases}Si_3O_8{\equiv}Na_2K\\ Si_3O_8{\equiv}Na_2K\\ Si_3O_8{\equiv}Na_2K\end{cases}$$

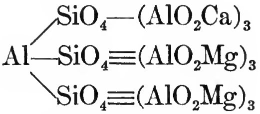
which leads to the subjoined comparison:

	Found.	Calculated.
SiO_2	59.25	59.79
Al_2O_3	12.57	12.74
FeO	.93	....
K_2O	5.37	5.85
Na_2O	7.63	7.72
Li_2O	9.04	9.34
F	7.32	7.88
	102.11	103.32
Less O	3.08	3.32
	99.03	100.00

In Flink's analysis of polylithionite from another locality potassium is in excess of sodium, but otherwise the ratios are nearly the same.

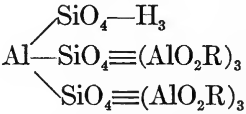
In the clintonite group or so-called "brittle micas" we have a series of highly basic compounds commonly free from alkalies. They are morphologically like biotite and are characterized by the presence of the univalent radicle AlO_2R'', R'' being either Mg, Ca, Fe'', or Mn. The most basic mica of the group, the end member of the series, is xanthophyllite, which has approximately the formula $Al(SiO_4)_3(AlO_2R'')_9$, with $R_9=Mg_6Ca_3$. In seybertite three of the univalent radicles are replaced by hydrogen, and in chloritoid there is still more replacement of a different kind. The ideal formulæ are as follows:

Xanthophyllite.



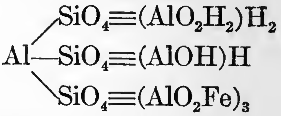
$$\mathrm{Al}\begin{cases}\mathrm{SiO_4-(AlO_2Ca)_3}\\ \mathrm{SiO_4\equiv(AlO_2Mg)_3}\\ \mathrm{SiO_4\equiv(AlO_2Mg)_3}\end{cases}$$

Seybertite.



$$\mathrm{Al}\begin{cases}\mathrm{SiO_4-H_3}\\ \mathrm{SiO_4\equiv(AlO_2R)_3}\\ \mathrm{SiO_4\equiv(AlO_2R)_3}\end{cases}$$

Chloritoid.



$$\mathrm{Al}\begin{cases}\mathrm{SiO_4\equiv(AlO_2H_2)H_2}\\ \mathrm{SiO_4\equiv(AlOH)H}\\ \mathrm{SiO_4\equiv(AlO_2Fe)_3}\end{cases}$$

In xanthophyllite there is always some hydration, and in the other species there are various small replacements of Al by Fe''', of Fe'' by Mn, etc., as in all the other micas. Ottrelite, a fourth member of the series, is like chloritoid, but contains Si_3O_8 instead of SiO_4; that is, its formula is trisilicate The pure theoretical compounds have the following composition:

	Xanthophyllite.	Seybertite.	Chloritoid.	Ottrelite.
SiO_2	16.45	21.53	23.81	48.38
Al_2O_3	46.37	42.70	40.48	27.42
FeO			28.57	19.36
MgO	21.91	19.14		
CaO	15.27	13.40		
H_2O		3.23	7.14	4.84
	100.00	100.00	100.00	100.00

Xanthophyllite decomposes on ignition into two portions—one soluble and the other insoluble in hydrochloric acid. The insoluble portion has the composition of spinel, a mineral which generally accompanies clintonite micas, and of which the formation is rendered intelligible by the formulæ.[1] The actual decomposition may perhaps be represented by the subjoined equation:

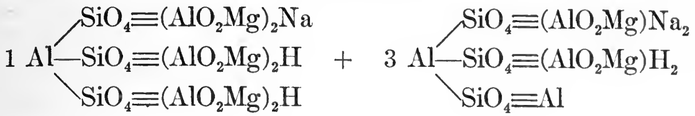
$$\overset{\textit{Xanthophyllite.}}{\mathrm{Ca_3Mg_6Al_{10}(SiO_4)_3O_{18}}}=\overset{\textit{Spinel.}}{\mathrm{4MgAl_2O_4}}+\overset{\textit{Garnet.}}{\mathrm{Al_2(SiO_4)_3Ca_3}}+\overset{\textit{Magnesia.}}{\mathrm{2MgO}}.$$

---

[1] For a different interpretation of these micas see the former edition of this memoir, U. S. Geol. Survey Bull. 125, 1895; also for details see Clarke and Schneider, U. S. Geol. Survey Bull. 113, p. 27, 1893.

The lime-alumina garnet and the free magnesia would constitute the soluble portion of the ignited mineral. The equation, of course, is purely hypothetical and would be difficult to verify experimentally.

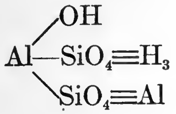
One other mineral, willcoxite, an alteration product of corundum, seems to be best classified with the clintonite micas. It appears to be a basic analogue of the mixed biotite-phlogopite kind, and its analysis gives quite sharply the subjoined formula:



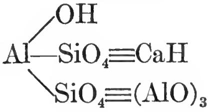
A little iron is present in the mineral and the sodium is partly replaced by potassium.

From some points of view kaolin may be regarded as a member of the mica series, especially when its crystalline form is considered. With it the calcium mica, margarite, which is commonly classed as a member of the clintonite group, can be conveniently correlated. Furthermore, margarite yields an alteration product, dudleyite, which falls into line with the other two species, thus:

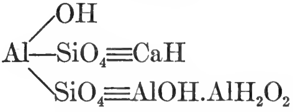
Kaolin.



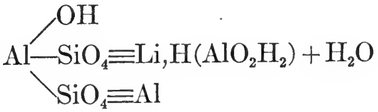
Margarite.



Dudleyite.



Cookeite, a micaceous mineral found associated with lepidolite and encrusting lithia tourmalines, also seems to belong here. Its formula is simply written



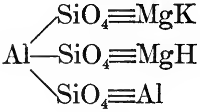
which agrees well with Penfield's analysis of the cookeite from Maine and Schaller's analysis of the California mineral.

	Penfield.	Schaller.	Calculated.
SiO_2	34.00	35.53	35.08
Al_2O_3	45.06	44.23	44.73
Fe_2O_3	.45	....	
CaO	.04	Trace.	....
Li_2O	4.02	2.73	4.40
Na_2O	.19	2.11	
K_2O	.14	.31	
H_2O	14.96	14.18	15.79
F	.46	1.46	
	99.32	100.55	100.00

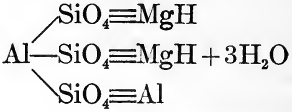
These expressions for kaolin and its analogues are suggestive but not altogether conclusive. They represent the known facts fairly well, however, and so serve their purpose for the time being.

By hydration, and sometimes by oxidation, the micas undergo alteration, yielding a great variety of products which are known in general as vermiculites. This is especially true as regards the ferro-magnesian micas, which lose alkalies and take up water with the greatest ease, in accordance with what seems to be a well-defined law. Thus we have

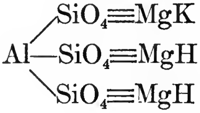
Biotite.



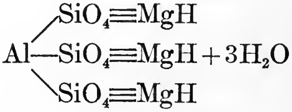
Hydrobiotite.



Phlogopite.



Hydrophlogopite.

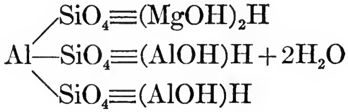


These micas occur in nature in great variety of admixture, and the corresponding vermiculites show a parallel complexity. In the normal series, however, the alteration commonly follows the line indicated by the formulæ, and the vermiculite is simply the mica with H in place of K or Na, plus 3 molecules of loosely combined water. Two of these molecules are, as a rule, given off at 100°, and regained in moist air, suggesting an analogy between the vermiculites and the zeolites. Some vermiculites are only monohydrated, and many of the so-called species which have received names are mere mixtures of altered and unaltered micas, representing stages of transition between the original mineral and the final product. Maconite, lucasite, and philadelphite are incompletely altered micas of this kind.

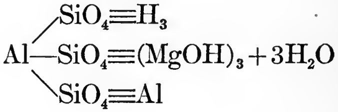
Jefferisite is quite near the normal hydrobiotite, kerrite approximates to a hydrophlogopite, and lennilite is a mixture between the two, but in all three of these minerals the hydration is somewhat irregular, and there are the usual replacements of aluminum and magnesium by ferric and ferrous iron.

In some of the vermiculites basic radicles appear, corresponding to the excesses of oxygen over the normal ratios that are found among the micas themselves. For example, roseite and protovermiculite may be written:

Roseite.



Protovermiculite.

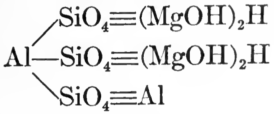


expressions which fit the actual analyses fairly well. Such formulæ, however, must be interpreted with much caution. They do not necessarily imply that these micas are definite compounds; they merely symbolize one kind of alteration to which the minerals of this group are subject. They mark a transition between the micas and the chlorites, and similar but more complex examples are found in hallite, painterite, pyrosclerite, vaalite, and pattersonite. Caswellite is another altered mica, rich in manganese and lime but of uncertain formula. Indeed, it is hardly worth while to write formulæ for these minerals, for none of them seems to be a single definite compound.

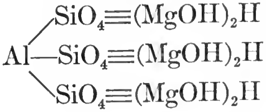
Between the micas and the more basic chlorites the relations are exceedingly close. All the species are foliated, all or nearly all are monoclinic, and to each of the ferromagnesian micas one or more chlorites, higher in magnesia and water, seem to correspond. The exact formulation of the chlorites, however, is not a simple matter. Some of the so-called "species" are not homogeneous; others are isomorphous mixtures; and in all of them replacements of one dyad base by another, or of aluminum by iron, occur. In the chlorites the basic univalent and bivalent groups $—Mg—OH$, $—Fe''—OH$, $—Al{=}(OH)_2$, $=Al—OH$, $—Fe'''{=}(OH)_2$, and $=Fe'''—OH$ appear, but their precise identification is complicated by uncertainties in the hydration of the minerals. In general, the water shown by the analyses is constitutional, but in some chlorites it may be extraneous, like the water of the zeolites. An exact study of the hydration of the chlorites by modern methods is yet to be made.

Some so-called chlorites, containing alkalies, are obviously mixtures of chlorites and micas, but the true species are all referable to the types of molecule represented by biotite and phlogopite except a few that fall more nearly into line with margarite and kaolin. Typical chlorites, which, however, are rarely if ever found pure, may be represented thus:

Biotite-chlorite.



Phlogopite-chlorite.



An average pennine contains these two molecules commingled in the ratio 1 : 1, whereas in clinochlore and leuchtenbergite the ratio is 2 : 3, with the second Al of the biotite formula replaced by 3AlO. That is, the formula of a typical clinochlore is represented by

$$3\ Al(SiO_4)_3(MgOH)_6H_3 + 2\ Al(SiO_4)_3(MgOH)_4H_2(AlO)_3.$$

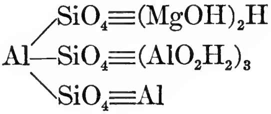
These expressions give the subjoined compositions for the two chlorites.

	Pennine.	Clinochlore.
SiO_2	34. 35	31. 58
Al_2O_3	14. 60	19. 65
MgO	38. 17	36. 49
H_2O	12. 88	12. 28
	100. 00	100. 00

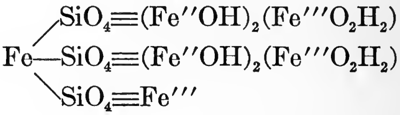
The mixtures may occur in other proportions; the magnesium may be partly replaced by iron, and in the varieties kammererite and kotschubeite some chromium, equivalent to aluminum, appears. A glance at the tables of analyses in the textbooks of Dana and Hintze will show how variable in composition these and other chlorites really are.

Three chlorites, rumpfite and the ferrosoferric minerals cronstedtite and melanolite, seem to conform very nearly to the biotite type of formula, thus—

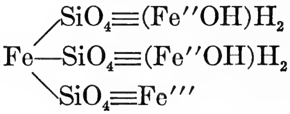
Rumpfite.



Cronstedtite.



Melanolite.



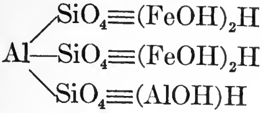
The composition of the three minerals, as given by these formulæ, is as follows:

	Rumpfite.	Cronstedtite.	Melanolite.
SiO_2	30. 20	20. 93	33. 70
Al_2O_3	42. 78	....	....
Fe_2O_3	....	37. 21	29. 63
FeO	....	33. 48	26. 67
MgO	13. 42	....	....
H_2O	13. 60	8. 38	10. 00
	100. 00	100. 00	100. 00

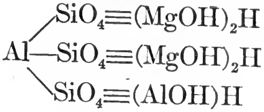
In melanolite a little ferric oxide is replaced by alumina.

The two species brunsvigite and delessite may be given either biotitic or phlogopitic formulæ, according to the character of the hydration. If one molecule of their water is zeolitic in character—that is, nonessential—the minerals are of the biotite type. If all the water is constitutional, they are related to phlogopite. Brunsvigite is essentially a ferrous chlorite, delessite is ferromagnesian, and the two species correspond to the two formulæ—

Brunsvigite.



Delessite.

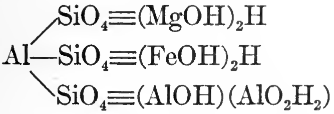


In delessite the magnesian end compound is sometimes nearly approached, but usually about one-fourth of the magnesium is replaced by iron, and a little ferric replacement of alumina is also common. Delessite is a very variable mineral. When computed with Mg_3Fe_1, its average composition is as follows, in comparison with brunsvigite:

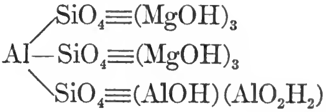
	Delessite.	Brunsvigite.
SiO_2	32.97	28.04
Al_2O_3	18.68	15.89
FeO	13.19	44.86
MgO	21.98	....
H_2O	13.18	11.21
	100.00	100.00

Closely related to the two preceding species are prochlorite and grochauite, to which the following structures may be assigned:

Prochlorite.



Grochauite.

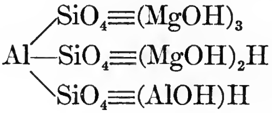


The composition of these two minerals is as follows:

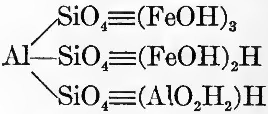
	Prochlorite.	Grochauite.
SiO_2	28.28	27.53
Al_2O_3	23.90	23.39
FeO	22.50	....
MgO	12.66	36.69
H_2O	12.66	12.39
	100.00	100.00

This prochlorite is fairly typical, but a so-called "prochlorite" from Culsagee, North Carolina,[1] is quite different in its ratios and contains very little iron. It is allied to metachlorite, as the following formulæ show:

Culsagee prochlorite.



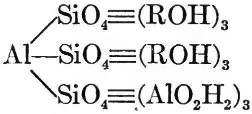
Metachlorite.



The percentage compositions are as follows:

	Culsagee prochlorite.	Metachlorite.
SiO_2	28.48	22.73
Al_2O_3	24.21	19.32
FeO		45.46
MgO	31.65	
H_2O	15.66	12.49
	100.00	100.00

Corundophilite is a chlorite with still higher alumina, which probably has the following constitution:



SiO_2	22.68
Al_2O_3	25.69
FeO	17.88
MgO	20.15
H_2O	13.60
	100.00

The calculated composition gives $R_6 = Mg_4Fe_2$. The water is a little too high, and may be partly vermiculitic. If so, $(AlO_2H_2)_3$ should be replaced by $(AlO)_3$, a replacement which may be desirable in some of the other formulæ already given. The need of investigating the hydration of the chlorites has already been pointed out, but it is well to emphasize it here.

Diabantite and thuringite appear to be mixed silicates, intermediate between the vermiculites and the chlorites, thus:

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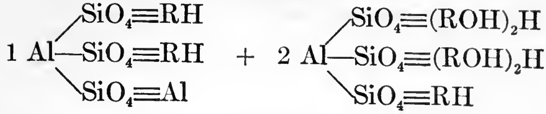
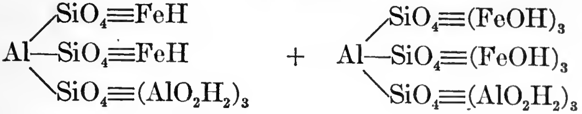
[1] Analyses 17–20 on p. 654 of Dana's System of mineralogy, 6th ed., 1892.

Diabantite.



$$1\ \mathrm{Al}\begin{cases}\mathrm{SiO_4{\equiv}RH}\\ \mathrm{SiO_4{\equiv}RH}\\ \mathrm{SiO_4{\equiv}Al}\end{cases} + 2\ \mathrm{Al}\begin{cases}\mathrm{SiO_4{\equiv}(ROH)_2H}\\ \mathrm{SiO_4{\equiv}(ROH)_2H}\\ \mathrm{SiO_4{\equiv}RH}\end{cases}$$

Thuringite.

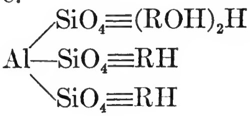


$$\mathrm{Al}\begin{cases}\mathrm{SiO_4{\equiv}FeH}\\ \mathrm{SiO_4{\equiv}FeH}\\ \mathrm{SiO_4{\equiv}(AlO_2H_2)_3}\end{cases} + \mathrm{Al}\begin{cases}\mathrm{SiO_4{\equiv}(FeOH)_3}\\ \mathrm{SiO_4{\equiv}(FeOH)_3}\\ \mathrm{SiO_4{\equiv}(AlO_2H_2)_3}\end{cases}$$

In diabantite $R_{12}=Mg_7Fe_5$, and in thuringite one-third of the aluminum is replaced by ferric iron. Hence the following compositions:

	Diabantite.	Thuringite.
SiO_2	34.93	22.78
Al_2O_3	13.19	19.37
Fe_2O_3	....	10.13
FeO	23.29	36.33
MgO	18.11	....
H_2O	10.48	11.39
	100.00	100.00

The talc-chlorite of Traversella is another intermediate compound simply formulated as shown below. In the actual mineral one-fifth of the dyad portion is Fe.

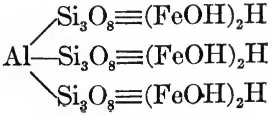


$$\mathrm{Al}\begin{cases}\mathrm{SiO_4{\equiv}(ROH)_2H}\\ \mathrm{SiO_4{\equiv}RH}\\ \mathrm{SiO_4{\equiv}RH}\end{cases}$$

SiO_2	39.00
Al_2O_3	11.04
FeO	12.47
MgO	27.75
H_2O	9.74
	100.00

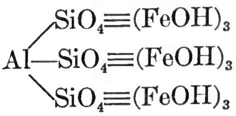
Stilpnomelane has a truly chloritic formula, but is distinct from the others in being a trisilicate. This is probably true also of the very uncertain ekmanite, which has a most variable composition. The two formulæ may be written thus:

Stilpnomelane.



$$\mathrm{Al}\begin{cases}\mathrm{Si_3O_8{\equiv}(FeOH)_2H}\\ \mathrm{Si_3O_8{\equiv}(FeOH)_2H}\\ \mathrm{Si_3O_8{\equiv}(FeOH)_2H}\end{cases}$$

Ekmanite.



$$\mathrm{Al}\begin{cases}\mathrm{SiO_4{\equiv}(FeOH)_3}\\ \mathrm{SiO_4{\equiv}(FeOH)_3}\\ \mathrm{SiO_4{\equiv}(FeOH)_3}\end{cases}$$

The theoretical composition follows:

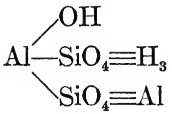
	Stilpnomelane.	Ekmanite.
SiO_2	48.91	40.91
Al_2O_3	4.62	3.86
FeO	39.13	49.09
H_2O	7.34	6.14
	100.00	100.00

Epichlorite appears to be a mixture of stilpnomelane with the equivalent magnesian orthosilicate, $Al(SiO_4)_3(MgOH)_6H_3$, in nearly equal percentages. The recently described minguetite[1] is apparently a mixture of stilpnomelane and a lepidomelane.

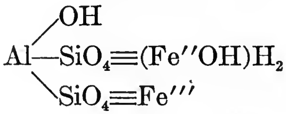
So far all the chlorites conform to the mica type of formula as represented by biotite and phlogopite. In general they may be regarded as salts of an alumosilicic acid, $Al(SiO_4)_3H_9$, and its corresponding trisilicate, in which the nine hydrogen atoms are replaceable by a variety of basic radicles. The apparent complexity of the chlorites vanishes and the relations between them become clear and simple.

There is, however, a group of chlorites of distinct character from the normal series. Like margarite they model after kaolin in the following manner:

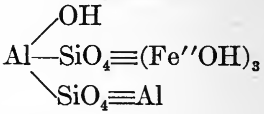
Kaolin.



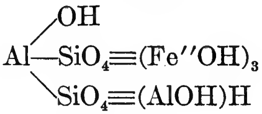
Strigovite.



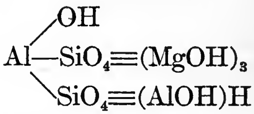
Aphrosiderite.



Daphnite.



Sheridanite.[2]



The theoretical composition of the four chlorites is therefore as follows:

	Strigovite.	Aphrosiderite.	Daphnite.	Sheridanite.
SiO_2	33.61	25.32	24.40	30.30
Al_2O_3	14.17	21.52	20.73	25.76
Fe_2O_3	22.22	....	....	....
FeO	20.00	45.57	43.90	....
MgO	....	....	....	30.30
H_2O	10.00	7.59	10.97	13.64
	100.00	100.00	100.00	100.00

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[1] Lacroix, Soc. min. Bull., vol. 33, p. 270, 1910.

[2] See Wolff, J. E., Am. Jour. Sci., 4th ser., vol. 34, p. 475, 1912.

Strigovite is the least satisfactory of these species, for the reason that the analyses are discordant. The formula given it in Dana may be written $AlOH(SiO_4)_2R.(ROH)_2H$, which, however, is of the same general type as that employed here.

Several other chloritic minerals have received names, such as chamosite, klementite, euralite, pycnochlorite, epiphanite, hullite, and chlorophæite, but they are not very well characterized. The analyses can all be interpreted in harmony with the other chlorites, but it is hardly worth while to discuss them in detail until the several minerals shall have been more thoroughly studied. Enough has been done to show that the micas, clintonites, vermiculites, and chlorites form one systematic group of minerals, and all the valid evidence is satisfied. The facts that garnet and vesuvianite alter into chlorites and that chloritic pseudomorphs after feldspar are known serve to connect still more closely the formulæ here adopted with the similar formulæ of the preceding groups of minerals.

When clinochlore or leuchtenbergite is strongly ignited, it yields, like xanthophyllite, a product insoluble in hydrochloric acid, having the composition of spinel. This reaction establishes still more definitely the relationship between the chlorites and the clintonite group, and it is readily intelligible in the light of the structural expressions. The splitting up, under influence of heat, of mixtures containing such groups of atoms as MgOH, AlOH, and AlO_2H_2 ought to generate spinel, and the appearance of a compound of this character is evidence in favor of the formulæ.

An interpretation of the chlorites proposed by Tschermak has had some acceptance, but the scheme is complicated and subject to very serious objections. According to Tschermak the "orthochlorites," which include pennine, clinochlore, prochlorite, and corundophilite, are molecular or crystalline mixtures of serpentine, $H_4Mg_3Si_2O_9$, and an uncertain substance, amesite, $H_4Mg_2Al_2SiO_9$, with the equivalent molecules containing iron. Now serpentine, on strong calcination, breaks up into water, olivine, and enstatite, the enstatite being insoluble in acids. But the magnesian chlorites, which, if Tschermak's theory were true, should yield about 18 per cent of enstatite on ignition, yield none at all. Spinel is formed instead of enstatite, and in quantities proportional to the excesses of oxygen over the orthosilicate ratio. That is, serpentine molecules are not present in the chlorites, and the Tschermak hypothesis breaks down.

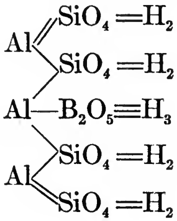
THE ALUMINOUS BOROSILICATES.

In this group of minerals, of which tourmaline is the most important, there are five species, namely, tourmaline, axinite, dumortierite, serendibite, and manandonite. There are also several borosilicates of the rare earths, which may properly be studied with them even though they contain no aluminum.

Although tourmaline in its several varieties is apparently quite complex, the evidence for its interpretation is abundant and ample. Its variations in composition are shown by numerous good analyses, its associations are well known, and its alteration products have been observed in a sufficient number of examples. From the minerals which have been discussed in the preceding chapters it differs essentially in that it contains boron, and the part played by this element is a new question to be interpreted.

When tourmaline undergoes alteration, the commonest product is a mica, and between the micas and the tourmalines there are very striking analogies. With the lithia micas, lithia tourmalines are generally associated; with muscovite and biotite, iron tourmalines occur; and magnesian tourmalines accompany phlogopite. In each case the composition of the tourmaline seems to bear a relation to that of the associated mica. Furthermore, the varieties of tourmaline shade one into another through an unbroken series of gradations, and this may happen to some extent in one and the same crystal. The genus tourmaline, in short, represents a series of compounds, and these are parallel to the normal mica series.

Upon the constitution of tourmaline there have been many essays written and much controversy. It is not necessary to discuss here the literature of the subject in detail, for only two types of formula are now seriously considered, and they differ principally in regard to the ratio between silicon and oxgyen. Penfield and Foote[1] represent the mineral as a salt of the acid $H_{11}Al_3B_2Si_4O_{21}$, which may be written structurally thus:



In this formula the boron appears as the radicle of an acid $H_4B_2O_5$, which is a rational compound. So far as its atomic ratios are concerned, the formula fits most of the published tourmaline analyses very well, although not all of them, but it does not suggest the well-known alterability of the mineral into mica. It is also difficult to apply in detail, that is, to apportion the several bases replacing hydrogen in any symmetrical manner, so as to indicate clearly the

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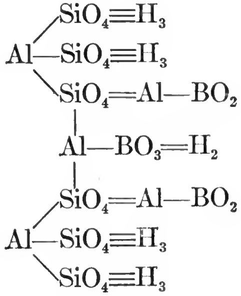
[1] Am. Jour. Sci., 4th ser., vol. 7, p. 97, 1899. Criticized by Clarke, idem, vol. 8, p. 111, 1899. Reply by Penfield, idem, vol. 10, p. 19, 1900.

end members of the series of compounds which are commingled in tourmaline. This difficulty has been avoided in part by later writers, notably by Schaller[1] and Reiner,[2] who triple the Penfield-Foote formula, so making the ultimate tourmaline acid $H_{60}Si_{12}B_6O_{63}$. From this both Schaller and Reiner derive a number of distinct compounds, which, as mixed crystals, make up tourmaline. The tripled formula, however, is unwieldy, and not easy to represent by a simple and presumably stable series of structures. This objection is entitled to some weight but is not necessarily fatal.

In the Penfield-Foote type of formula the silicon-boron-oxygen ratio is represented by $Si_4B_2O_{21}$, which is equivalent to $Si_6B_3O_{31.5}$. In the tourmaline formulæ proposed in the former edition of this memoir the nucleus $Si_6B_3O_{31}$ appears, with an oxygen ratio slightly lower than that of Penfield and Foote. In general the Penfield-Foote formula fits the actual analyses a little better than mine, but the difference is very slight and suggests a possible constant error. Heretofore all analyses of tourmaline have been made upon finely ground material, and fine grinding is accompanied by more or less adsorption of water from the air. It also leads to some oxidation of ferrous iron, a change which takes place very easily in tourmaline, and these two almost certain sources of error tend to raise the oxygen ratio in the minerals as analyzed. These sources of error were not known when the published analyses were made and must now be taken into account.

Now, the foregoing considerations being kept in mind, and also the alterability of tourmaline into mica, the following formula for the fundamental tourmaline acid seems to be probable:



This involves the lowest observed ratio between aluminum and silicon, and also the constant ratio between silicon and boron. The boron is shown as partly metaborate and partly orthoborate, which may be regarded as improbable. As an alternative the boron may be represented as the quinquivalent group B_3O_7, the radicle of a possi-

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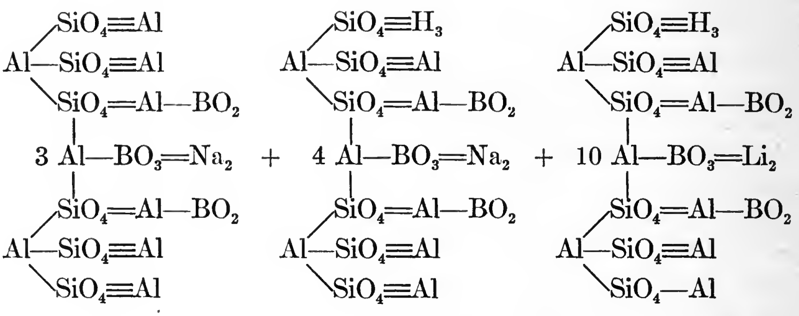
[1] Zeitschr. Kryst. Min., vol. 51, p. 321, 1913.

[2] Inaugural Dissertation, Heidelberg, 1913. Reiner gives a good summary of earlier work on the subject. His formulæ are those of Wülfing.

ble acid $H_5B_3O_7$, a rational compound. But many tourmalines contain fluorine, and some analyses show a deficiency of boron, which is not always ascribable to analytical error. Fluorine in such tourmalines may perhaps replace the BO_2 group, a supposition for which there are good arguments, although it may not be absolutely proved. To this point reference will be made later.

In the proposed tourmaline acid various replacements of hydrogen are possible, by means of which the individual tourmalines, as mixed crystals, can be quite accurately formulated. At one end of the series, with the group Al_5Si_6, we find some magnesia and iron tourmalines, at the other end, approaching the ratio Al_9Si_6, are the colored lithia tourmalines. Of the lithia tourmalines the extreme member known is the rubellite from Elba, which approximates in composition to the following mixture of molecules:



This may be compared with Schaller's analysis of the mineral[1] thus:

	Found.	Calculated.
SiO_2	37.89	38.08
B_2O_3	10.28	11.06
Al_2O_3	43.85	43.98
Ti_2O_3	.04	....
FeO	.11	....
MnO	.11	....
CaO	.07	....
Na_2O	2.43	2.69
Li_2O	1.66	1.85
H_2O	3.47	2.34
F	.10	....
	100.01	100.00

The differences here are mainly due to the water and to the small neglected impurities. The water found is probably too high, because

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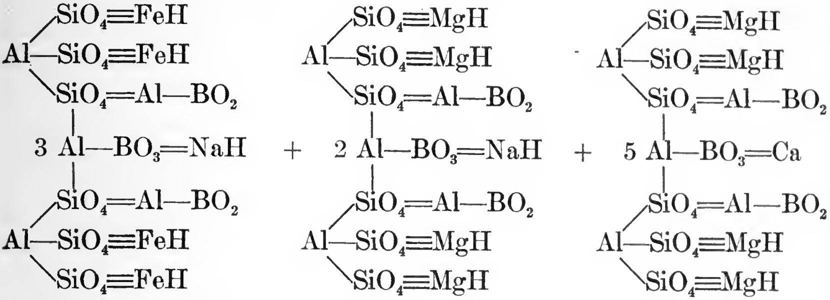
[1] All the analyses of tourmaline cited here were made in the laboratory of the United States Geological Survey.

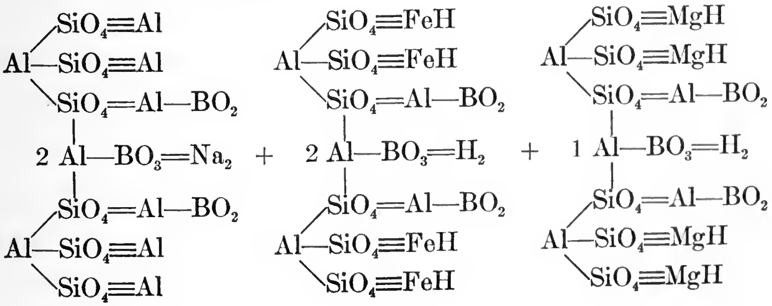
of fine grinding. The comparison is also influenced by the fact that the mixed molecules are not exactly represented by such simple numbers as are assumed in this computation. The latter consideration applies throughout the discussion.

At the other end of the series we have the magnesian tourmaline from Pierrepont, New York, as analyzed by Riggs. The mixed molecules are nearly as follows:



	Found.	Calculated.
SiO_2	35.61	35.91
TiO_2	.55	....
B_2O_3	10.15	10.48
Al_2O_3	25.29	25.44
Fe_2O_3	.44	....
FeO	8.19	8.62
MgO	11.07	11.17
CaO	3.31	2.79
Na_2O	1.51	1.55
K_2O	.20	....
H_2O	3.34	4.04
F	.27	....
	99.93	100.00

An interesting intermediate tourmaline is the black variety from Lost Valley, California, analyzed by Schaller. Its formula is that of a mixed crystal, as follows:



	Found.	Calculated.
SiO_2	35. 96	35. 87
B_2O_3	10. 61	10. 42
Al_2O_3	33. 28	33. 43
Ti_2O_3	. 36	....
FeO	11. 04	11. 43
MnO	. 13	....
CaO	. 42	....
MgO	3. 48	3. 18
Na_2O	2. 16	2. 46
H_2O	3. 31	3. 21
	100. 75	100. 00

It is not necessary to give more examples of tourmaline formulæ, for all tourmalines are represented by the type of structure proposed here. The alkali tourmalines tend toward the more aluminous end of the series, the magnesian and iron tourmalines toward the less aluminous. All the tourmalines now known are evidently mixed crystals, but the complexity of the mixtures is more apparent than real. Whether any tourmalines contain ferric iron is still uncertain, but the probabilities are adverse to its presence. It appears in many analyses, but that is probably due to oxidation, so that the minerals analyzed were not quite normal. Ferric tourmalines are theoretically possible, but their existence is unproved. The iron of tourmaline is at least predominatingly ferrous.

The formulæ for tourmaline adopted here not only express the composition of the mineral but also indicate its obvious relation to the micas and its ready alterability into them. A molecule of tourmaline, with elimination of boric acid and one atom of aluminum, splits into two molecules of the mica type, and the transformation is easily understood. Potash is of course taken up. Certain experiments by Lemberg,[1] who investigated the action of alkaline solutions upon tourmaline, are in accord with these suppositions.

Although otherwise interpreted by Brögger, the minerals cappelinite, melanocerite, karyocerite, and tritomite seem to be chemically akin to tourmaline. This view of their nature has already been suggested by Wiik,[2] and it is sustained both by chemical and by morphological considerations. Cappelinite is hexagonal, and the other species, like tourmaline, are rhombohedral. They are silicates of rare earths, which are mostly trivalent, like aluminum; all contain boron, and all but cappelinite contain fluorine also. Furthermore, all four species, considered together, illustrate the reciprocity between boric acid and fluorine, which has been suggested in the discussion of tourmaline. Thus, if we compute the atomic ratios from the analyses cited by Brögger,[3] the following relation appears:

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[1] Deutsche geol. Gesell. Zeitschr., 1892, p. 239.

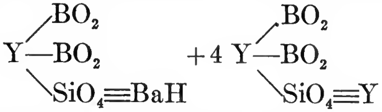
[2] Zeitschr. Kryst. Min., vol. 23, pp. 421, 422, 1894.

[3] Zeitschr. Kryst. Min., vol. 16, pp. 462–469, 1890.

	Si.	B.	F.	B+F.
Cappelinite	236	488	....	488
Melanocerite	218	92	304	396
Karyocerite	216	134	296	430
Tritomite	226	210	226	436

That is, Si : B+F : : 1 : 2 nearly, variations being due to the fact that in the first three minerals the boric acid was determined by difference, and also, probably, to the occasional replacement of fluorine by hydroxyl. Another source of variation is found in the presence of tetrad bases, as will be seen later, but for the moment the relation indicated seems to be reasonably clear.

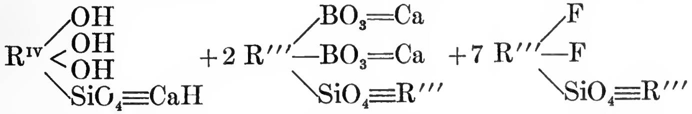
The first number of the group, cappelinite, is a borosilicate of yttrium and barium and approximates in composition to



$$Y\begin{array}{l}\diagup BO_2\\ -BO_2\\ \diagdown SiO_4\equiv BaH\end{array}+4\,Y\begin{array}{l}\diagup BO_2\\ -BO_2\\ \diagdown SiO_4\equiv Y\end{array}$$

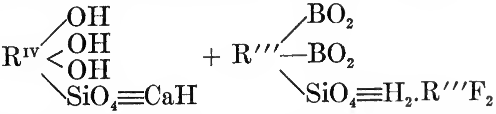
With the earths of uncertain molecular weight, designated as "yttria," are a little lanthanum oxide and trifling quantities of ThO_2 and CeO_2, and with the barium are some calcium and alkalies.

The other three members of the group are all more complicated than cappelinite, and vary from it in type by containing tetrad oxides, such as CeO_2, ThO_2, and ZrO_2. In eudialyte and catapleiite we have two rhombohedral silicates of zirconia, which help to explain these compounds. Catapleiite probably has the constitution $(OH)_3Zr.Si_3O_8.R'_3$. If we regard the tetrad bases in the cappelinite group as forming orthosilicates of this same type, the remainder of each mineral may be written as a mixture of molecules like those already designated, but with cerium earths predominating over yttrium, and fluorine replacing some boric radicles. Thus, melanocerite is not far from



$$R^{IV}\begin{array}{l}\diagup OH\\ < OH\\ \;\;\, OH\\ \diagdown SiO_4\equiv CaH\end{array}+2\,R'''\begin{array}{l}\diagup BO_3=Ca\\ -BO_3=Ca\\ \diagdown SiO_4\equiv R'''\end{array}+7\,R'''\begin{array}{l}\diagup F\\ -F\\ \diagdown SiO_4\equiv R'''\end{array}$$

Karyocerite may be written similarly, and tritomite becomes



$$R^{IV}\begin{array}{l}\diagup OH\\ < OH\\ \;\;\, OH\\ \diagdown SiO_4\equiv CaH\end{array}+R'''\begin{array}{l}\diagup BO_2\\ -BO_2\\ \diagdown SiO_4\equiv H_2.R'''F_2\end{array}$$

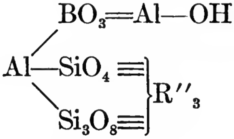
These formulæ are uncertain and need verification with material from other sources. At present they have only a reasonable probability. The tetrad silicate in them, however, will be seen to be highly probable when we come to the discussion of the other allied compounds in their proper connection later.

The second aluminous borosilicate, axinite, is difficult to interpret structurally, for the reason that its relations to other species and its modes of alteration have not been definitely traced. It is, however, easily formulated empirically and is well represented as a varying mixture of two molecules:

Ferroaxinite	$HFeCa_2Al_2BSi_4O_{16}$
Manganaxinite	$HMnCa_2Al_2BSi_4O_{16}$

A little magnesia is also shown in the analyses of axinite, which points to the probable existence of a magnesium salt exactly equivalent to the others. A distinctly magnesian axinite, however, has not yet been found.[1]

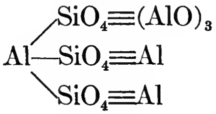
The formulæ given above seem to make axinite an orthosilicate, provided that the boron is regarded as basic and equivalent to aluminum. But boron is distinctly an acid-forming element, and therefore it is more probable that in axinite it has acid functions. On this supposition its structural formula may be best written as a mixed orthosilicate and trisilicate, thus:



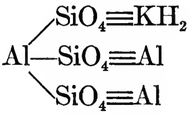
in which $R''_3 = (Fe, Mn)_1\ Ca_2$, the calcium being constant. Other structures are possible, but no one seems to have any advantage over this. Until further evidence is discovered the proposed expression may be regarded as valid, but it represents only the composition of the mineral, and nothing more. It is, however, in conformity with the general theory of substitution.

Dumortierite is much more easily interpreted than axinite. It is related to andalusite, with which it is often associated, and it alters into muscovite. Its composition has been determined by the careful analyses of Ford[2] and Schaller,[3] and is simply represented by a significant constitutional formula. By slightly modifying Schaller's formula the following comparison is obtained:

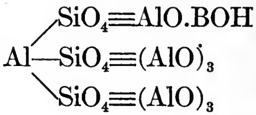
Andalusite.



Muscovite.



Dumortierite.



The bivalent group =B—OH is evidently equivalent to the corresponding aluminum group. Schaller prefers to write it as two radicles, H and —B=O, and his form may perhaps be better.

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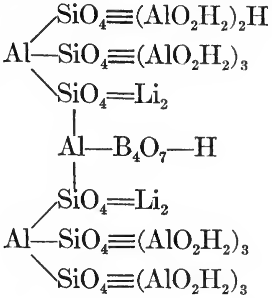
[1] For a full discussion of the composition of axinite see Schaller, U. S. Geol. Survey Bull. 490, p. 37, 1911. See also the former edition of this memoir, U. S. Geol. Survey Bull. 125, 1895.

[2] Am. Jour. Sci., 4th ser., vol 14, p. 426, 1902.

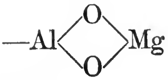
[3] U. S. Geol. Survey Bull. 262, p. 91, 1905.

The mineral manandonite, recently described by Lacroix,[1] is also easily formulated. As written by Lacroix, in close agreement with the analysis, its empirical formula is $H_{24}Li_4Al_{14}B_4Si_6O_{63}$, a highly basic compound. Regarding the boron as present in the group B_4O_7, the well-known radicle of borax, manandonite may be given the following structure, having some analogy to that of tourmaline:

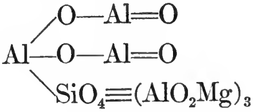


This formula needs to be confirmed by more analyses, and an investigation as to the relations of manandonite to other species.

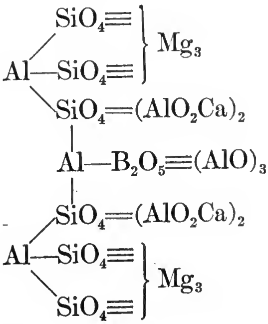
One other borosilicate, serendibite, has been described by Prior and Coomáraswámy,[2] who assign to it the empirical formula $10RO.5Al_2O_3.B_2O_3.6SiO_2$, in which RO is partly CaO and partly MgO, with a little FeO. In composition it has some analogy to tourmaline, and it also resembles the ultrabasic silicate sapphirine. The latter mineral is akin to the brittle micas, in which the univalent group



appears, and its formula may be



although that is not quite certain. With these clues the formula of serendibite may be written thus:



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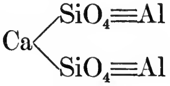
[1] Soc. Min. Bull., vol. 35, p. 223, 1912.

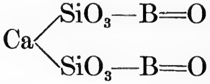
[2] Mineralog. Mag., vol. 13, p. 224, 1903.

which fairly satisfies the known conditions. This formula, however, like some of the others, can only be regarded as tentative.

Although it contains no alumina, danburite, $CaB_2Si_2O_8$, is perhaps most conveniently considered here. It is sometimes regarded as the equivalent of barsowite, $CaAl_2Si_2O_8$, a doubtful isomer of anorthite. But barsowite gelatinizes with hydrochloric acid, whereas danburite is attacked by the reagent only after ignition. Possibly the difference may be as follows:



$$\mathrm{Ca}\begin{cases}\mathrm{SiO_4{\equiv}Al}\\ \mathrm{SiO_4{\equiv}Al}\end{cases}$$



$$\mathrm{Ca}\begin{cases}\mathrm{SiO_3{-}B{=}O}\\ \mathrm{SiO_3{-}B{=}O}\end{cases}$$

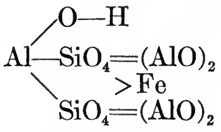
danburite being a metasilicate. Other formulæ are also possible, and more data are needed before any conclusion can be reached. The associations of danburite with feldspars, mica, pyroxene, etc., suggest that it may be a pseudometasilicate, allied in structure to the aluminous constituent of augite.

MISCELLANEOUS SPECIES.

Among the orthosilicates and trisilicates of aluminum, ferric iron, and other triad elements, there are a considerable number which do not fall conveniently into any of the preceding groups of minerals, or which are doubtful as regards their genetic affinities. Some of them have obvious relationships to other species, and some are quite obscure in character, but all seem to be conformable to the theory of substitution.

First in order of importance is the mineral staurolite, a highly basic silicate, which is evidently akin to andalusite and sillimanite, and which, like them, is orthorhombic. Like andalusite, furthermore, staurolite alters to muscovite, an entire crystal becoming transformed throughout into an aggregate of mica scales.

By far the best evidence as to the composition of staurolite is that furnished by the analyses of Penfield and Pratt,[1] who adopt Groth's formula, $HAl_5Fe''Si_2O_{13}$. This, structurally, may be written



$$\mathrm{Al}\begin{cases}\mathrm{O{-}H}\\ \mathrm{SiO_4{=}(AlO)_2}\\ \qquad\qquad >\mathrm{Fe}\\ \mathrm{SiO_4{=}(AlO)_2}\end{cases}$$

which expresses a partial relation to the micas, andalusite, and so on. The theoretical percentage composition calculated from this formula agrees well with the results of analysis, except that it gives the silica nearly 1 per cent too low, a discrepancy which Penfield and Pratt attribute to inclusions of silica in the minerals analyzed.

By means of a slightly different formula the relations of staurolite to the other species can be much more clearly shown, but it assumes

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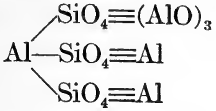
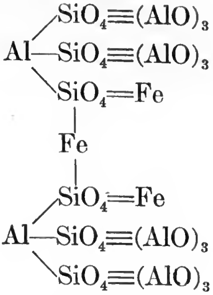
[1] Am. Jour. Sci., 3d ser., vol. 47, p. 81, 1894.

that the ideal staurolite is not yet known. The expressions proposed are as follows:

Andalusite.



Staurolite.

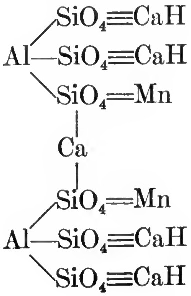


This formula, in contrast with that of Penfield and Pratt, and with their reduced analysis of staurolite from Lisbon, New Hampshire, gives the following percentage composition:

	Lisbon.	Penfield and Pratt.	New formula.
SiO_2	27.44	26.32	27.90
Al_2O_3	55.16	55.92	55.35
FeO	15.72	15.79	16.75
H_2O	1.68	1.97	....
	100.00	100.00	100.00

If, now, we assume that the actual staurolite is slightly altered by hydration, some Fe being replaced by H_2 and by FeOH+H, the discrepancies between formula and analyses are sufficiently accounted for. The new formula is more symmetrical than the old one; it better expresses the alterability of staurolite into muscovite; and it seems to satisfy the evidence with sufficient completeness. When we remember that staurolite is excessively liable to inclusions and alterations, a very sharp agreement between analysis and theory is not to be expected.

Still another orthorhombic species, harstigite, has a formula analogous in some ways to that of staurolite. For harstigite there is but one analysis extant, which gives nearly



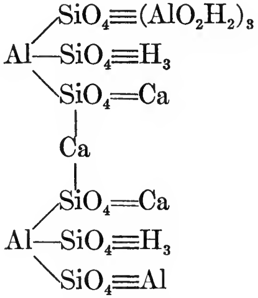
This, in comparison with Flink's analysis, gives the following percentage composition:

	Found.	Calculated.
SiO_2	38.94	39.13
Al_2O_3	10.61	11.09
MnO	12.81	15.43
MgO	3.27	
CaO	29.23	30.44
K_2O	.35	
Na_2O	.71	
H_2O	3.97	3.91
	99.89	100.00

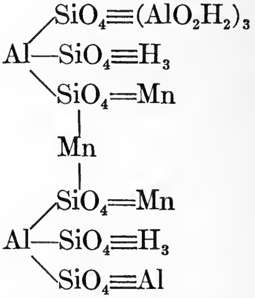
This result is fairly satisfactory. More data relative to harstigite are evidently needed.

Two closely related silicates, the calcic lawsonite and the manganous carpholite, may perhaps be analogous in structure to staurolite and harstigite. For both minerals the simplest empirical formula is $H_4R''Al_2Si_2O_{10}$, which, tripled, can assume the following form:

Lawsonite.

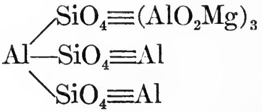


Carpholite.



Lawsonite is orthorhombic. The isometric hibschite seems to have the same composition, but is too incompletely known to be satisfactorily discussed here.

An interesting pair of ultrabasic silicates is furnished by the species kornerupine (or prismatine) and grandidierite. Both are orthorhombic; kornerupine alters into kryptotile, and grandidierite yields a similar and perhaps identical derivative. To kornerupine the empirical formula Al_2MgSiO_6 has been commonly assigned, which, tripled, may be written:

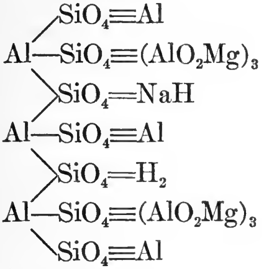


in close analogy to andalusite and kryptotile. The recent investigation of prismatine by Uhlig,[1] however, shows that the mineral is more complex and in better agreement with the formula

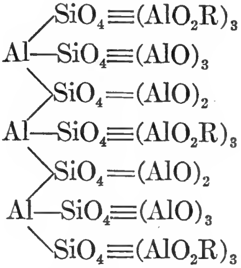
$$NaH_3Mg_6Al_{12}Si_7O_{40}.$$

Grandidierite,[2] described by Lacroix in 1902, has the empirical formula $R''_9(Al, Fe)_{22}Si_7O_{56}$, with aluminum largely predominant over iron. R'' is mainly magnesium, but with some replacement by iron, calcium, and a little sodium. That is, it is a mixed crystalline mineral, but of fairly definite type. Both species, with the empirical formulæ now given them, are expressible by analogous structures, thus·

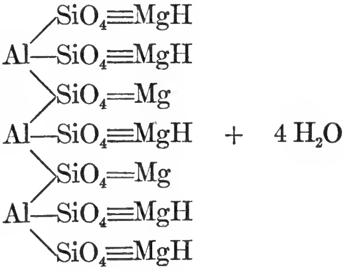
Kornerupine.



Grandidierite.



The nacreous or micaceous mineral batavite[3] is perhaps of similar type, although Weinschenk has assigned it the relatively simple formula, $4H_2O.4MgO.Al_2O_3.4SiO_2$. Its composition, however, is equally well expressed as follows:



Batavite, like many other minerals, needs further investigation, as the following comparison between analysis and formulæ clearly shows:

	Found.	Calculated.	
		Weinschenk.	New formula.
SiO_2	42.33	41.81	43.30
Al_2O_3	16.35	17.77	15.78
MgO	28.17	27.88	28.86
H_2O	13.19	12.54	12.06
	100.04	100.00	100.00

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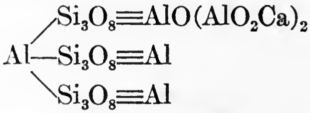
[1] Zeitschr. Kryst. Min., vol. 47, p. 215, 1910.

[2] Soc. min. Bull., vol. 25, p. 85, 1902; vol. 27, p. 259, 1904.

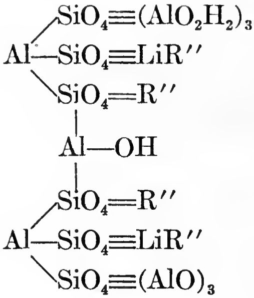
[3] Zeitschr. Kryst. Min., vol. 28, p. 160, 1897.

A still more unusual type of silicate is presented by didymolite, a mineral recently described by Meister,[1] who assigns it the formula $2CaO.3Al_2O_3.9SiO_2$. Constitutionally this seems to be a basic derivative of a trisilicic anorthite, with the following structure:



To bityite, a mineral from the tourmaline region of Madagascar, described by Lacroix,[2] may be assigned the empirical formula $H_7Li_2GlCa_3Al_9Si_6O_{34}$.

This leads to a structural formula analogous to that of tourmaline, which suggests that bityite may be an intermediate compound between tourmaline and cookeite.



The comparison between analysis and formula is as follows:

	Found.	Calculated.
SiO_2	31.95	32.58
Al_2O_3	41.75	41.54
CaO	14.30	15.20
MgO	.13	
GlO	2.27	2.26
Li_2O	2.73	2.72
Na_2O	.40	
K_2O	.16	
H_2O	6.50	5.70
	100.19	100.00

The water found is probably a little too high, due either to alteration or perhaps to fine grinding. Tourmaline, manandonite, serendibite, and bityite seem to be closely related species.

The vanadiosilicate or arseniosilicate, ardennite, is a compound of quite different type from any so far considered. It is a mixed silicate

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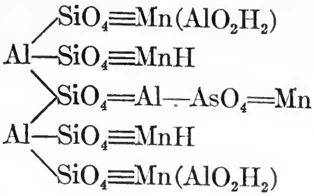
[1] Neues Jahrb., 1912, vol. 1, ref. 403.

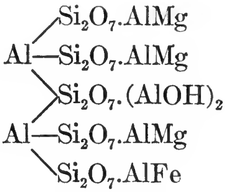
[2] Soc. min. Bull., vol. 31, p. 241, 1908.

in which sometimes the vanadic radicle predominates and sometimes the arsenical group, but the structure of the molecule is the same in both varieties. According to Prandtl[1] its empirical formula is $H_6Mn_5Al_5(As,V)Si_5O_{28}$, which can be written structurally as follows:



The vanadic ardennite is strictly isomorphous with the arsenical compound and in it V replaces As.

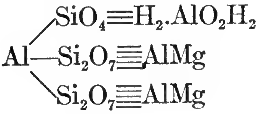
Among the silicates of aluminum, salts of orthodisilicic acid are very rare. The only one which seems to be thoroughly defined is iolite, which agrees best with the formula



which requires the following percentage composition:

SiO_2	49.26
Al_2O_3	33.50
MgO	9.85
FeO	5.91
H_2O	1.48
	100.00

in close concordance with the best recorded analyses. By alteration iolite passes into mica, going through an intermediate stage, however, known as chlorophyllite. This substance may be regarded as formed by hydration, in which the linking group of Si_2O_7 in iolite is split into two orthosilicic radicles, yielding two molecules of the type



from which the final transition into a mica is easy. If we take Rammelsberg's analysis of chlorophyllite, recalculate the ferric oxide into

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[1] Zeitschr. Kryst. Min., vol. 40, p. 392, 1905.

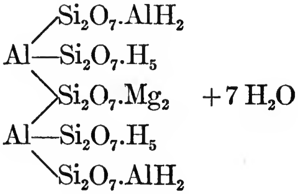
alumina and lime into magnesia, reducing afterward to 100 per cent, we get the following comparison between observed fact and the composition of chlorophyllite computed from the foregoing formula:

	Found.	Reduced.	Calculated.
SiO_2	46.31	47.99	48.39
Al_2O_3	25.17	33.34	32.90
Fe_2O_3	10.99		
MgO	10.91	11.74	12.90
CaO	.58		
H_2O	6.70	6.93	5.81
	100.66	100.00	100.00

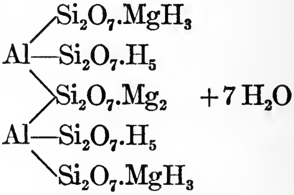
The agreement is as close as could be reasonably expected. The replacement of a little magnesia by a little water in the original alteration product accounts for the discrepancies.

Two other magnesian alumosilicates, of rather uncertain character, may possibly be related to iolite; namely, the lasallite of G. Friedel[1] and the pilolite of Heddle.[2] Both minerals are highly hydrous and are fairly represented by the subjoined formulæ:

Lasallite.

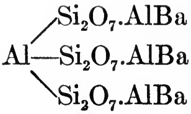


Pilolite.



The exact hydration is doubtful but not far from that shown in the formulæ. There are a number of other questionable minerals recorded,[3] of generally similar composition, but their consideration in detail would hardly be profitable. Some of them are probably mixtures of magnesian silicates with clays.

Two more aluminous minerals are probably to be classed as orthodisilicates. One barylite, is near



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[1] Soc. min. Bull., vol. 24, p. 12, 1901; idem, vol. 30, p. 80, 1907.

[2] Min. Mag., vol. 2, p. 206, 1878.

[3] See Dana's System of mineralogy, 6th ed., pp. 705–711, 1892.

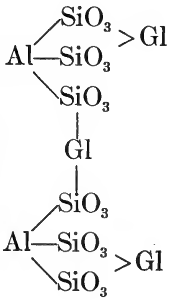
which requires the following percentage composition:

SiO_2	35.19
Al_2O_3	19.94
BaO	44.87
	100.00

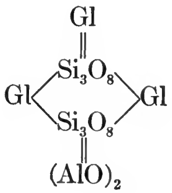
The other silicate, sphenoclase, is approximately $Al_2(Si_2O_7)_3Ca_6$, which may be analogous to barylite in structure or written as a calcium salt similar in type to okenite. Both barylite and sphenoclase, however, are uncertain, and their relations are not definitely known.

Well-defined metasilicates of aluminum, or alumometasilicates, seem to be few in number. It has already been shown that many of the species classed as metasilicates are really mixed salts, trisilicates and orthosilicates being commingled.

With beryl, however, $Gl_3Al_2Si_6O_{18}$, the evidence in favor of a metasilicate structure is fairly good, although the composition can also be expressed as that of a basic trisilicate. There are thus two alternatives,



and



But beryl alters into mica, a fact which is favorable to the first of these formulæ, and all of its commoner alterations seem to take place by replacement of glucinum. In the trisilicate formula the alumina should be equally replaceable, and so far the evidence is adverse to it. Furthermore, Traube[1] has effected the synthesis of beryl by precipitating a mixture of glucinum and aluminum sulphates with a solution of sodium metasilicate, and then crystallizing by fusion of the precipitate with boron trioxide. Since the starting point was a metasilicate, there is a fair presumption that the product was a metasilicate also. Beryl can be written as a pseudometasilicate, but there are no data to justify doing so.

The mineral astrolite, described by Reinisch[2] may perhaps be a metasilicate. If so its formula is $(Na,K)Fe''(AlFe''')(SiO_3)_5.H_2O$, but the species needs further study. Spodumene and jadeite also have apparently metasilicate ratios, but on mineralogic grounds it is best

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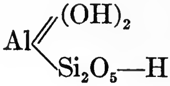
[1] Neues Jahrb., 1884, vol. 1, p. 275.

[2] Centralbl. Mineralogie, 1904, p. 108.

to defer their consideration and to take them up in connection with the pyroxenes and amphiboles.

The alumosilicates derived from metadisilicic acid, $H_2Si_2O_5$, are few in number. Two of them, ptilolite and mordenite, have already been discussed as zeolites; two others, petalite and milarite, demand attention now. The formula of petalite, empirically, is $AlLi(Si_2O_5)_2$, similar to the metasilicate formula for spodumene, and the two species are commonly associated. Petalite, however, has far the lower density of the two and is therefore presumably composed of smaller molecules. An alteration product of petalite, hydrocastorite, approximates roughly



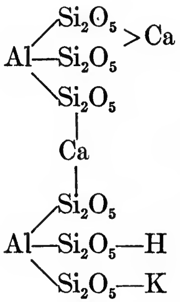
$$\mathrm{Al}\begin{cases}(\mathrm{OH})_2\\ \mathrm{Si_2O_5{-}H}\end{cases}$$

which requires the following percentage composition:

SiO_2	60.60
Al_2O_3	25.75
H_2O	13.65
	100.00

The actual hydrocastorite contains about 4.3 per cent of lime, and is doubtless impure. By Doelter[1] petalite is interpreted somewhat differently, being given the empirical formula $Al_2Li_2Si_{10}O_{24}$, but the formula here adopted is the one most generally received.

Milarite, $HKCa_2Al_2(Si_2O_5)_6$, is, like beryl, hexagonal, and its formula is analogously to be written



$$\begin{array}{l}\mathrm{Al}\begin{cases}\mathrm{Si_2O_5}\\ \mathrm{Si_2O_5}\\ \mathrm{Si_2O_5}\end{cases}\!\!>\mathrm{Ca}\ \text{(first two)}\\ \qquad\ \ |\\ \qquad\mathrm{Ca}\\ \qquad\ \ |\\ \mathrm{Al}\begin{cases}\mathrm{Si_2O_5}\\ \mathrm{Si_2O_5{-}H}\\ \mathrm{Si_2O_5{-}K}\end{cases}\end{array}$$

For this species the only evidence is that of its composition. Its genesis and its possible alterations are unknown.

The clays are peculiarly difficult to interpret constitutionally. One member of the group, kaolin, has already been considered, and this member is peculiar in being crystalline. The other clays are amorphous and of uncertain origin; they often occur in complicated mixtures, are difficult to identify with certainty, and still more difficult

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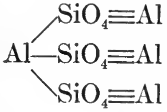
[1] Min. pet. Mitt., 1878, p. 529.

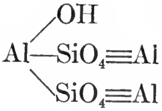
to correlate with other species. They undoubtedly represent the breaking down of crystalline silicates, to which they are related somewhat as kaolin is related to the feldspars, but rarely, if ever, has their actual genesis been observed. Furthermore, the integrity of some of the clay silicates is in question. According to Stremme[1] several of them are merely mixtures of colloidal alumina and colloidal silica, whereas Thugutt[2] regards them as definite compounds. The controversy can probably be settled only by careful thermal investigation as to the character of the hydration, a line of attack which has been followed to some extent by Le Chatelier,[3] although not yet to a finality. The formulæ proposed here are therefore to be regarded as merely tentative and as a first step toward the better study of the several species.

Upon comparing the formula of aluminum orthosilicate with that of kaolin an indication of serial arrangement becomes evident, which may be written thus:

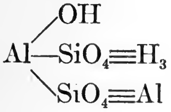
Normal salt.



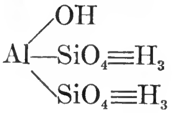
Westanite or woerthite.



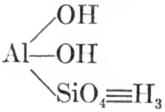
Kaolin.



Montmorillonite.



Newtonite.



Woerthite is an altered sillimanite, and westanite is perhaps a similar derivative of andalusite. The newtonite compound has already appeared in the mica series among the components of cookeite and rumpfite.

The best that can be said for these formulæ is that they are suggestive. In one respect they are highly questionable, for the reason that the group $-SiO_4\equiv H_3$ is indicative of loosely combined water, whereas in these particular clays the water is quite firmly retained. On this point much fuller information is needed, and future evidence may prove that the serial relation indicated is apparent only.

The composition of rectorite may be $Al_3(SiO_4)_3H_3 + 2H_2O$, or that of a hydrous kryptotile. Halloysite has the composition of kaolin plus one molecule of water, the latter being removable at or about 100°. Halloysite, however, differs from kaolin in being decomposable by hydrochloric acid, and hence it is unlikely that the two species

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[1] Centralbl. Mineralogie, 1911, p. 205.

[2] Idem, 1911, p. 97; 1912, p. 35.

[3] Zeitschr. physikal. Chemie, vol. 1, p. 396, 1887.

have similar structure. Allophane is perhaps $(AlO_2H_2)_2H_2SiO_4+3H_2O$ or it may be written analogously to andalusite,

$$Al_3(SiO_4)_3(AlO_2H_2)_3.12H_2O.$$

Neither formula is sustained by any good evidence. Other clays are possibly as follows:

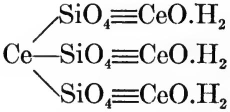
Samoite	$Al_4(SiO_4)_3.10H_2O$
Cimolite	$Al_4(Si_3O_8)_3.6H_2O$
Collyrite	$(AlO)_4SiO_4.6H_2O$
Schrötterite	$(AlO_2H_2)_4SiO_4.6H_2O$
Melite	$(AlO_2H_2)_4SiO_4.4H_2O$

One other member of this group, termierite, has the empirical formula $Al_2Si_6O_{15}.18H_2O$. It may be a metadisilicate, but until the exact character of its hydration is determined its constitution must remain in doubt.

None of these formulæ can be construed as anything more than a temporary suggestion, which may help research. The hydrous ferric silicates are, if anything, less satisfactory than the aluminum salts. Anthosiderite is representable by the formula $Fe_4(Si_3O_8)_3.2H_2O$, and chloropal by the expression $Fe_2(SiO_4)_3H_6$. Nontronite, according to Weinschenk,[1] is the ferric equivalent of kaolin, $H_4Fe_2Si_2O_9$, but Bergeat,[2] who has studied the mineral as a derivative of kaolinite, assigns it the more complex formula $H_8Fe_4Si_9O_{28}$. Müllerite is probably a metasilicate, $Fe_2(SiO_3)_3.2H_2O$. Hisingerite seems to range from a ferric kaolin to a ferric halloysite, and further than this it is not worth while to go. The remaining iron clays which have received specific names are altogether doubtful. The chromium clays, wolchonskoite, alexandrolite, and others, are also of very uncertain character.

Several silicates of the rare earths may be properly mentioned here on account of their analogy to the alumosilicates.

To cerite, which is of doubtful composition, the provisional formula



may be assigned. Other earth metals—lanthanum, the two didymiums, and others—replace a considerable part of the cerium. With cerium only the formula requires the following percentage composition:

SiO_2	20.22
Ce_2O_3	73.71
H_2O	6.07
	100.00

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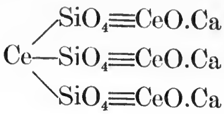
[1] Zeitschr. Kryst. Min., vol. 28, p. 150, 1897.

[2] Centralbl. Mineralogie, 1909, p. 161.

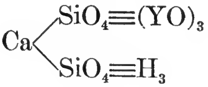
Beckelite is perhaps similar to cerite in structure, having the probable formula



$$\mathrm{Ce}\begin{array}{l}\diagup\mathrm{SiO_4{\equiv}CeO.Ca}\\ -\mathrm{SiO_4{\equiv}CeO.Ca}\\ \diagdown\mathrm{SiO_4{\equiv}CeO.Ca}\end{array}$$

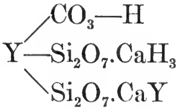
with lanthanum, neodymium, praseodymium, and other elements partly replacing cerium.

The yttrium silicate, thálenite, is possibly represented by the simple formula $\mathrm{Y{\equiv}SiO_4{-}R'}$, in which R' is partly H and partly Na or K. The ideally pure mineral, however, is yet to be found. Another silicate of yttrium and calcium, hellandite, is of quite different type, and agrees well with the formula



$$\mathrm{Ca}\begin{array}{l}\diagup\mathrm{SiO_4{\equiv}(YO)_3}\\ \diagdown\mathrm{SiO_4{\equiv}H_3}\end{array}$$

Another yttrium mineral, cenosite or kainosite, appears to be an orthodisilicate containing a carbonic radicle, thus:



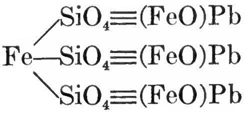
$$\mathrm{Y}\begin{array}{l}\diagup\mathrm{CO_3{-}H}\\ -\mathrm{Si_2O_7.CaH_3}\\ \diagdown\mathrm{Si_2O_7.CaY}\end{array}$$

The recently described thortveitite[1] is much simpler, being the normal orthodisilicate of scandium,

$$\mathrm{Sc_2Si_2O_7}$$

Britholite and erikite are phosphatosilicates, but the published analyses correspond to no simple formulæ. All these species need fuller investigation.

Several salts of triad bases may be noted here as having more analogy to the compounds of aluminum than to any other silicates. Melanotekite, for instance, is a silicate of lead and ferric iron, which, according to Warren,[1] has the empirical formula $\mathrm{Pb_4Fe_3Si_3O_{15}}$. Structurally this becomes



$$\mathrm{Fe}\begin{array}{l}\diagup\mathrm{SiO_4{\equiv}(FeO)Pb}\\ -\mathrm{SiO_4{\equiv}(FeO)Pb}\\ \diagdown\mathrm{SiO_4{\equiv}(FeO)Pb}\end{array}$$

Kentrolite is probably similar, but with Mn''' replacing Fe'''.

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[1] See Schertelig, Centralbl. Mineralogie, 1911, p. 721.

[2] Am. Jour. Sci., 4th ser., vol. 6, p. 116, 1898.

Glauconite, $FeK(SiO_3)_2.nH_2O$, is a hydrous silicate which is rarely found in even approximate purity. The formula, therefore, merely represents the best evidence we have as to the constitution of the mineral. It may be a pseudometasilicate and equivalent to a hydrated potassium acmite, a supposition which would seem to be capable of experimental verification. Some iron is commonly replaced by aluminum and some potassium by other basic radicles. Glauconite is of marine origin, but celadonite, formed by alteration in certain volcanic rocks, is probably the same compound.

Pseudobrookite is an orthotitanate of iron, $Fe_4(TiO_4)_3$, and arizonite is the metatitanate, $Fe_2(TiO_3)_3$. There are also the bismuth silicates, eulytite and agricolite, $Bi_4(SiO_4)_3$, which differ in form but are identical in empirical composition. They therefore suggest two types of chemical structure among the silicates of trivalent bases.

CHAPTER IV.

SILICATES OF DYAD BASES.

ORTHOSILICATES.

Although the orthosilicates of the dyad metals are presumably simpler than those of aluminum, the problem of their constitution, studied in the light of mineralogic evidence, is peculiarly difficult. Starting points exist, in the salts of magnesium, iron, manganese, zinc, and glucinum, but the derivatives are fewer than in the case of aluminum, and the evidence upon which to base argument is correspondingly limited.

Expressed in the simplest terms, the normal orthosilicates of this group are represented by the general formula R_2SiO_4. To this type the following minerals correspond:

Forsterite	Mg_2SiO_4
Fayalite	Fe_2SiO_4
Tephroite	Mn_2SiO_4
Willemite	Zn_2SiO_4
Phenakite	Gl_2SiO_4
Monticellite	$CaMgSiO_4$
Knebelite	$MnFeSiO_4$
Glaucochroite	$CaMnSiO_4$

Between these minerals there are many intermediate species or varieties, which may be either isomorphous mixtures or double salts representing polymers of the fundamental type. Thus, chrysolite or olivine[1] may be a mixture of forsterite and fayalite, or, in the case of hyalosiderite, a salt of the formula $Mg_4Fe_2(SiO_4)_3$. So also, allied to knebelite, we have igelströmite, $Fe_4Mn_2(SiO_4)_3$, and in trimerite we find the salt $Gl_3Mn_2Ca(SiO_4)_3$.

A close study of the derivatives of these normal salts shows that the assumption of polymerization seems to be necessary. If the theory of substitution is valid, then the existence of polymers must be taken for granted, and it thus becomes possible to develop a system of formulæ which satisfies all the conditions imposed by the evidence now at hand. For some of the species already mentioned the degree of polymerization is difficult to determine, and synthetic investigations seem to be needed. In other cases the problem is comparatively simple, and the indications as to the true formulæ are apparently clear.

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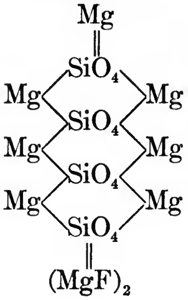
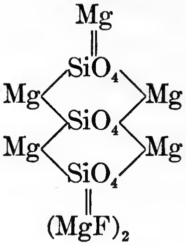
[1] Tschermak regards olivine as a basic metasilicate, but that interpretation is difficult to reconcile with all the evidence.

For instance, a good example is furnished by the chondrodite group, for which we have the empirical formulæ established by Penfield and Howe.[1] Structurally written these become

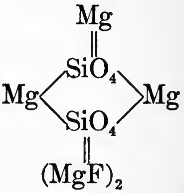
Clinohumite.



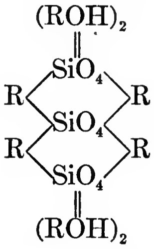
Humite.



Chondrodite.



or derivatives respectively of the salts $Mg_8(SiO_4)_4$, $Mg_6(SiO_4)_3$, and $Mg_4(SiO_4)_2$, with one atom of magnesium in each case replaced by the two univalent —Mg—F groups. Prolectite is a fourth member of the series, described by Sjögren,[2] which, on crystallographic grounds, is supposed to be simply $Mg{=}SiO_4{=}(MgF)_2$, although it has not been analyzed. The fluorine in these minerals is usually replaced in part by hydroxyl, but the replacement is rarely complete. The mineral leucophœnicite[3] is a similar compound, with a formula analogous to that of humite, namely, $Mn_5(SiO_4)_3(MnOH)_2$, but containing slight replacements of manganese by calcium and zinc. Gageite is also a member of the humite group, and its formula can be written



in which R represents Zn, Mg, Mn, in the ratio 1 : 3 : 7. It is closely related to leucophœnicite.[4]

Clinohedrite occurs in association with forsterite, and the two species have nearly the same specific gravity. Hence forsterite may be $Mg_8(SiO_4)_4$, and this is the only datum available from which to infer its molecular magnitude. The synthetic transformation of forsterite into clinohumite, if it could be effected, would go far toward settling the question.

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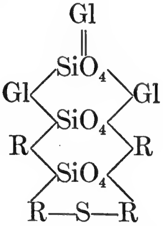
[1] Am. Jour. Sci., 3d ser., vol. 47, p. 188, 1894.

[2] Geol. Inst. Upsala Bull., vol. 1, p. 40, 1892–93; idem, vol. 2, p. 99, 1894–95.

[3] See Penfield and Howe, Am. Jour. Sci., 4th ser., vol. 8, p. 351, 1899.

[4] Phillips, Am. Jour. Sci., 4th ser., vol. 30, p. 283, 1910.

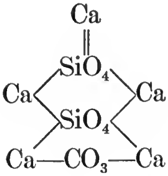
In the case of phenakite the triple formula $Gl_6(SiO_4)_3$ is rendered probable by the existence of trimerite, $Gl_3Mn_2Ca(SiO_4)_3$. It is also emphasized by the species helvite and danalite, which contain sulphur, probably combined in the dyad group —R—S—R—. Both these species, in all their known occurrences, agree with the general formula



in which R may be either Fe'', Mn, or Zn. The R is variable, but the other constituents are constant. In helvite, manganese and iron occur, and in danalite zinc appears. In the Colorado danalite zinc predominates largely over iron, and there is very little manganese. The Rockport danalite has iron in excess of zinc, and rather more manganese. The Cornish danalite is very low in zinc, and the iron largely exceeds the manganese. The ratio $Gl:SiO_4::3:3$, however, holds for all.

If phenakite is $Gl_6(SiO_4)_3$, then willemite, which is morphologically similar, is probably $Zn_6(SiO_4)_3$, with zinc partly replaced by manganese in the variety known as troostite.

Spurrite,[1] empirically $2Ca_2SiO_4.CaCO_3$, may possibly be assigned a structure similar in type to those used in the preceding groups of minerals, thus:



but with no evidence to go upon other than its composition. To the associated hillebrandite the formula $Ca_2SiO_4.H_2O$ has been given, but the water in it may be constitutional. In that case hillebrandite becomes a basic metasilicate, $(CaOH)_2SiO_3$. Molybdophyllite, $PbMgSiO_4.H_2O$, may be similarly constituted.

The three orthorhombic species, bertrandite, calamine, and ilvaite, are most conveniently represented as derivatives of the bipolymer $R_4(SiO_4)_2$, like chondrodite. Crystallographically ilvaite resembles

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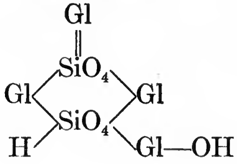
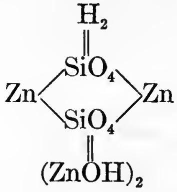
[1] See Wright, F. E., Am. Jour. Sci., 4th ser., vol. 26, p. 547, 1908.

humite, but bertrandite and calamine are related to each other. The simplest analogous formulæ for the three minerals are as follows:

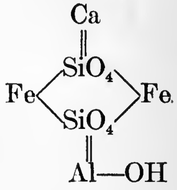
Bertrandite



Calamine.



Ilvaite.



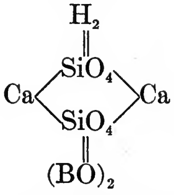
Calamine may also be written as a metasilicate, $(ZnOH)_2SiO_3$, with half of the formula indicated above, but then the analogy with bertrandite disappears. The structure proposed is therefore preferable, at least until more evidence has been accumulated. Clinohedrite is equivalent to calamine, but with half the zinc replaced by calcium. Zambonini [1] interprets calamine as a basic orthodisilicate. Baschieri [2] regards ilvaite also as an orthodisilicate. It is not easy to write constitutional formulæ for these minerals and to show their relation to other species on that basis. Further investigation is evidently needed.

To the datolite group a similar constitution is ascribable. The species, reduced to their simplest empirical expressions, are these:

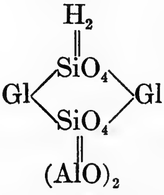
Datolite	$HCaBSiO_5$
Homilite	$Ca_2FeB_2Si_2O_{10}$
Euclase	$HGlAlSiO_5$
Gadolinite	$Gl_2FeY_2Si_2O_{10}$

By doubling the formulæ of datolite and euclase all four of the minerals become similar in constitution. Hydrogen here is evidently basic, and boron must play the same part as aluminum and yttrium. Assuming these elements to be present in the univalent groups BO, AlO, and YO, the subjoined formulæ follow:

Datolite.



Euclase.



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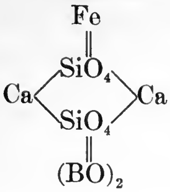
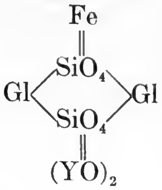
[1] Contributo allo studio dei silicati idrati, 1908.

[2] Zeitschr. Kryst. Min., vol. 49, p. 112, 1911.

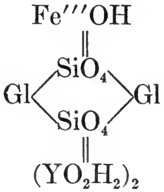
Homilite.



Gadolinite.



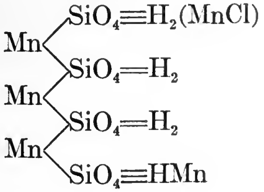
Gadolinite alters with great ease, passing by hydration into a brownish-red earthy substance. The analyses of this substance, which is probably never pure and definite, are not altogether satisfactory, but they indicate in a general way a transformation into the compound



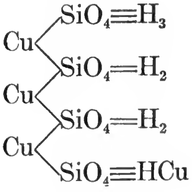
to which the alteration product very roughly approximates.

It will be observed that all of the foregoing structural formulæ in this group of compounds are rings or series of rings. From them, however, chainlike molecules are derivable, and these seem to exist in friedelite, pyrosmalite, and dioptase. The last-named mineral, simply written, is CuH_2SiO_4, but it is morphologically related to the two other species, which have a much greater complexity of composition. The following expressions derived from the polymer $R_8(SiO_4)_4$ are probably the best to represent existing evidence:

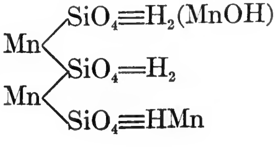
Friedelite.



Dioptase.

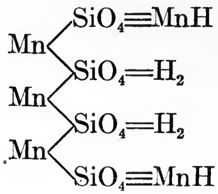


Pyrosmalite is like friedelite, but a large part of the manganese is replaced by iron. Possibly karyopilite may be similar, having the formula



These formulæ are purely tentative and need additional support. By synthetic and genetic investigations they may be supported or overthrown. That they sustain one another and fit in well with the formulæ of the preceding species is all that can be said in their favor. Palache[1] and Zambonini[2] assign more complex formulæ to friedelite. The chlorine in that mineral seems to be partly replaced by hydroxyl.

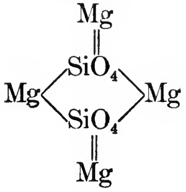
Bementite is still another silicate of similar type. In accordance with the latest analysis by Steiger,[3] its formula is simply written:



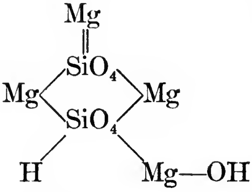
For serpentine, $H_4Mg_3Si_2O_9$, several formulæ are possible, and concerning them there has been much discussion. The species commonly originates in nature from the alteration of olivine on the one hand and from pyroxene or amphibole on the other, and it is therefore conceivable that it may include two or more isomeric compounds. In favor of this supposition there is some evidence but nothing conclusive. Massive serpentine, chrysotile, antigorite, and other allied varieties differ in their physical properties and suggest the existence of isomers, but much more investigation is needed in order to decide whether the supposition is true or not.

By some authorities serpentine is regarded as an orthosilicate and by others as a salt of the acid $H_6Si_2O_7$. On the latter supposition it becomes $Mg{=}Si_2O_7{\equiv}H_2(MgOH)_2$, which may be derived either from $2Mg_2SiO_4$ or $2MgSiO_3$, with loss of magnesium in one case and gain in the other. On the orthosilicate basis it is simply derivable from the polymer $Mg_4(SiO_4)_2$ and is related to the intermediate alteration product, villarsite, as follows:

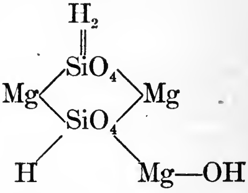
$Mg_4(SiO_4)_2$.



Villarsite.



Serpentine.



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[1] Am. Jour. Sci., 4th ser., vol. 29, p. 177, 1910.

[2] Contributo allo studio dei silicati idrati, 1908.

[3] See Palache, idem, p. 182.

On this scheme the formula for serpentine corresponds with that of chrondrodite; and the fact that the latter mineral alters readily into serpentine is strong evidence in its favor. In short, that formula best indicates the genetic relationships of serpentine, and on such grounds is preferable to the alternative diorthosilicate expression. The latter is not disproved; it is simply rendered less advantageous as regards existing evidence, which is the evidence now to be interpreted.

In some former investigations, carried on jointly with Dr. Schneider,[1] I sought to obtain experimental data in support of the orthosilicate formula here assigned to serpentine. By acting on serpentine with dry gaseous hydrochloric acid we found that a part of the magnesium could be removed as chloride, whereas olivine and the magnesian micas were not attacked. At first it seemed probable that the reaction would give a quantitative measure of the magnesium combined as MgOH; but our later experiments and those of Lindner [2] have shown that the expectation was not well founded. I still believe, however, that the reaction discriminates between those magnesium silicates which contain MgOH and those which contain Mg and H combined otherwise, for only the members which must belong to the first class are acted upon by the reagent. Brauns's objections [3] to this supposition, on the ground that the dry hydrochloric acid becomes moist, are not well taken, for the reaction always took place at temperatures lower than those at which water is given off. His criticisms may apply to the later stages of the reaction, after it has once fairly begun, but not to its initiation. The magnesian micas which contain several per cent of water are all decomposable by aqueous hydrochloric acid, but are scarcely touched by the dry gas; whereas, on the other hand, serpentine and the chlorites are strongly attacked. After the gaseous acid has acted it becomes moist, but very slowly, and most of the moisture is carried past the mineral under investigation before it has had time to produce an appreciable effect. It is possible, however, that a slow stream of the acid may act differently from a rapid current, and that the discordant results of observation may be due to differences of this kind.

When serpentine is ignited water is expelled, and a residue having the composition $Mg_3Si_2O_7$ is left behind. According to Rammelsberg [4] the water is given off in two portions—one-half upon weak

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[1] U. S. Geol. Survey Bull. 78, p. 11, 1891; Bull. 90, p. 11, 1892; and Bull. 113, pp. 27 and 34, 1893.

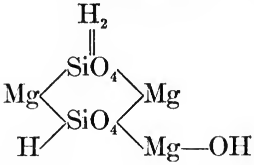
[2] A. Lindner, Inaugural Dissertation, Breslau, 1893.

[3] Neues Jahrb., 1894, vol. 1, p. 205.

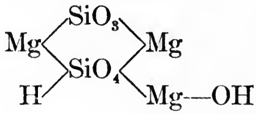
[4] Handbuch der Mineralchemie, 2d ed., p. 506, 1875.

ignition, the other after heating more strongly. On the orthosilicate theory these stages may be represented thus:

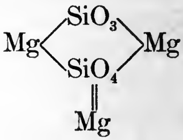
Serpentine.



First stage.

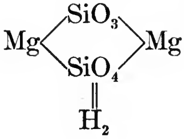


Second stage.



At the end of the second stage, if the ignition has not been too intense, the residue is still decomposable by hydrochloric acid, but by prolonged heating it is broken up quantitatively into soluble olivine and insoluble enstatite.

Allied to serpentine is the somewhat doubtful picrosmine, to which the formula $Mg_2H_2Si_2O_7$ is commonly assigned. Although this expression suggests a diorthosilicate, it may also be written



which represents picrosmine as a dehydrated serpentine altered subsequently by rehydration, with replacement of one magnesium atom by two of hydrogen. This mode of interpretation brings the mineral into line with serpentine, and all the known relations of the species are adequately expressed.

Several other hydrous silicates seem to belong in this group, but their nature is altogether doubtful. Thus we have

Aphrodite	$Mg_2H_4(SiO_4)_2$
Kerolite	$Mg(SiO_4)_2H_5(MgOH)$

Nepouite, $H_4Ni_3Si_2O_9$, seems to be the nickel equivalent of serpentine. Garnierite and noumeite, other hydrous silicates of nickel, are too variable in composition to be definitely classed.

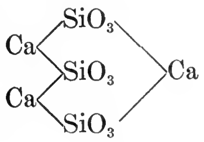
METASILICATES.

Although the metasilicates appear at first sight to be extremely simple, they are actually rather difficult to interpret. It is easy enough to deduce their empirical formulæ and to write them afterwards in structural terms, but this is not sufficient. The structural formulæ must express all known relations for each species, and in attempting to satisfy the established conditions the difficulties begin to appear. In the first place, metasilicic acid itself is defectively known, and no ester of the form R_2SiO_3 has yet been certainly obtained. Troost and Hautefeuille's ester $(C_2H_5)_8Si_4O_{12}$ suggests the possibility that metasilicic acid, like metaphosphoric acid, may polymerize, but an attempt to draw general conclusions on so important a question from one datum only would be most unwise. The possibility of polymeric acids, however, was clearly shown in the general discussion of the silicic acids in Chapter II of this bulletin. It is also emphasized by the existence of four distinct modifications of magnesium metasilicate, as proved by Allen, Wright, and Clement.[1] Whether these modifications represent different metasilicic acids or not is yet to be discovered.

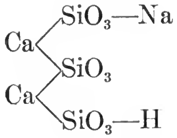
Again, as we have repeatedly seen, a mineral may be apparently a metasilicate and yet really a mixture of orthosilicates and trisilicates. Even a basic trisilicate can have seemingly metasilicate ratios. All these considerations complicate the identification and study of the true metasilicates to such an extent that only provisional conclusions can be drawn from the data now on hand.

A crystallized silicate of sodium, $Na_2SiO_3.8H_2O$, is well known. A solution of this salt added to a solution of calcium chloride precipitates a compound which, dried over sulphuric acid, has, according to my own observations, the composition $Ca_2Si_2O_6.5H_2O$. This, minus the water, is analogous to the mineral wollastonite, from which another mineral, pectolite, is derived. If wollastonite, instead of the formula $Ca_2Si_2O_6$ be given the formula $Ca_3Si_3O_9$, it may be compared structurally with pectolite, as follows:

Wollastonite.



Pectolite.



It must be remembered that the molecular weights of the inorganic silicates are not known but only assumed; and the problem suggested by the foregoing expressions is to find a set of structural formulæ which shall represent all the available evidence. Now, wollastonite is commonly classed with the pyroxenes, on crystallographic grounds; and so too is pectolite. But both species are very easily decomposed by even dilute and weak acids, whereas the normal pyroxenes are quite refractory, and, furthermore, wollastonite has a lower density than any pyroxene which approaches it in composition. Chemically, then, these species are dissimilar, and it is very doubtful whether they can properly be grouped together. That wollastonite and pectolite are true metasilicates, however, is sustained by the fact that when

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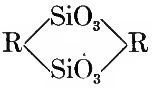
[1] Am. Jour. Sci., 4th ser., vol. 22, p. 385, 1906.

pectolite is ignited one-sixth of the silica, proportional to the hydrogen of the mineral, is split off in the free state and can be determined quantitatively. That is, two molecules of pectolite are decomposed with liberation of metasilicic acid, H_2SiO_3, which, in turn, divides into $SiO_2 + H_2O$. In some varieties of pectolite manganese replaces part of the calcium, and schizolite is a mineral of similar composition but with different ratios, its formula approximating $H_3Na_3Ca_3Mn_2(SiO_3)_8$. Schizolite, however, may be an isomorphous mixture of two silicates and not a simple compound. It is in no true sense equivalent to pectolite.

Empirically the nonaluminous pyroxenes resemble wollastonite in their ratios. Thus we have, according to the commonly accepted formulæ developed by Tschermak, Doelter, and others:

Enstatite, orthorhombic	$Mg_2Si_2O_6$
Diopside, monoclinic	$CaMgSi_2O_6$
Hedenbergite, monoclinic	$CaFeSi_2O_6$
Rhodonite, triclinic	$Mn_2Si_2O_6$

There is also a great number of other intermediate species or isomorphous mixtures in the pyroxene series, such as bronzite, hypersthene, schefferite, sahlite, jeffersonite, and fowlerite, in which we find, variously replacing one another, salts of magnesium, calcium, iron, manganese, and zinc. All these minerals, however, conform to the general formula $RSiO_3$, or $R_2Si_2O_6$, which adequately expresses their constitution so far as they alone are concerned. This formula can be written structurally—



which would be satisfactory if the pyroxene series ended here and if the amphiboles were unknown.

Going a step further we find in augite a pyroxene containing aluminum and having an oxygen ratio greater than in the group SiO_3. In place of aluminum ferric iron also occurs, and alkalies are sometimes present. Leaving these variations out of account, for consideration later, we have in augite, as interpreted by Tschermak, together with the normal compound $R_2Si_2O_6$, the basic salt RAl_2SiO_6. This substance, however, is not known by itself, unless it is represented by kornerupine, although the latest analysis of that mineral tends to negative the supposition. An artificial silicate of similar type, $K_2Al_2SiO_6$ has been prepared by Weyberg,[1] and may serve to strengthen Tschermak's assumption. This salt constitutionally may be regarded as a basic orthosilicate—

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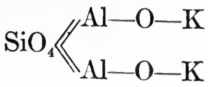
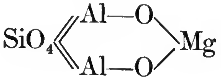
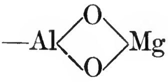
[1] Centralbl. Mineralogie, 1911, p. 326.



and its magnesian equivalent as



but neither expression is to be taken as final. The excess of oxygen in the pyroxenes may be due, with equal probability, to the equivalent group

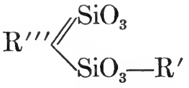


which has been assumed in preceding sections of this memoir.

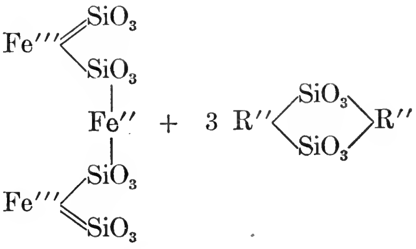
Still another series of silicates containing triad bases and also alkalies are classed with the pyroxenes, as follows:

Spodumene	$AlLiSi_2O_6$
Jadeite	$AlNaSi_2O_6$
Acmite	$Fe'''NaSi_2O_6$

and their empirical formulæ are fairly satisfactory. Structurally these expressions become, as metasilicates,



and babingtonite, which contains no alkalies, is similar, thus:

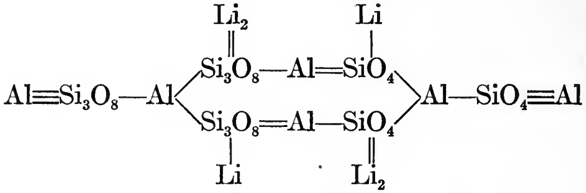


R'' being =Ca, Fe'', and Mn. The ferric molecule is evidently equivalent to two acmite molecules, with Na_2 replaced by a linking atom of iron.

So far, except partially in the comparison between wollastonite and pectolite, the formulæ cited for the pyroxenes express composition and composition only. But spodumene, as shown by the elaborate research of Brush and Dana, splits up on alteration into a mixture of eucryptite, an orthosalt, and albite, a trisilicate. This observation suggests two alternatives: Either that spodumene is derived from a polymetasilicic acid, or else that it is a pseudometasilicate, a mixed ortho- and tri-salt, like some of the species which have already been explained. An analogy with leucite, for example, will at once be inferred, and that species, empirically, is strikingly like spodumene, thus:

Leucite	$AlKSi_2O_6$
Spodumene	$AlLiSi_2O_6$

Like spodumene, leucite alters into a feldspar and a member of the nepheline group, but it differs from spodumene in form and in density. The specific gravity of the isometric leucite is 2.5, that of the monoclinic spodumene is nearly 3.2, and hence we may reasonably infer that spodumene has the larger and more condensed molecule. In order to explain the relations of leucite, its empirical formula was quadrupled, and in that way a relation with the garnet group was brought out. For spodumene, regarding it also as a mixed silicate, a sixfold multiplication of its formula indicates its greater density, and its splitting up into eucryptite and albite, with partial replacement of lithium by sodium, is representable as follows:

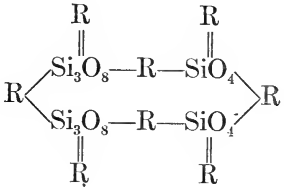


From this grouping of atoms the transition into $Al_3(Si_3O_8)_3Na_3 + Al_3(SiO_4)_3Li_3$ is hardly more than simple cleavage, and the relations between the three species are intelligibly expressed. Acmite, which yields pseudomorphs of analcite, and jadeite, also, probably follow the same rule, the formula of one being typical of the others. The ferric molecule in babingtonite should be still another instance of the same kind, with Fe''_3 in place of Li_6, and Fe''' instead of Al. Possibly pyrophyllite, $HAlSi_2O_6$, is related to spodumene and jadeite, much as kaolinite is related to the feldspars. Pyrophyllite is probably a pseudometasilicate, for silica is not liberated from it upon ignition, at least not to any noteworthy extent.

If the formula just developed for spodumene should be sustained, it would seem necessary to adjust the other pyroxenes with it. For Tschermak's aluminous constituent of augite this adjustment is easily made by taking the formula Al_2MgSiO_6 six times, as was done for spodumene. The parallelism between the two species is then representable as follows:

Spodumene	$Al_6(Si_3O_8)_3(SiO_4)_3Li_6$
Aluminum-augite	$Al_6(SiO_4)_3(SiO_4)_3(AlO_2Mg)_6$

the univalent AlO_2Mg having been recognized among the micas. This formula serves to explain the well-known alterability of augite into epidote and into mica, and so far at least is useful. I do not, however, feel inclined to put very much stress upon it, for as yet it is only an expression of analogy, which may or may not prove to be valid. It would seem to require the recognition of all the pyroxenes as pseudometasilicates, in which case the normal series, containing only dyad bases, would become



where four atoms of R are given linking functions, and the other four are, so to speak, replaceably combined. On this basis we should write

Diopside	$Mg_4Ca_4(Si_3O_8)_2(SiO_4)_2$
Hedenbergite	$Fe_4Ca_4(Si_3O_8)_2(SiO_4)_2$

The formula $R''_4(AlO)_8(SiO_4)_2(SiO_4)_2$ would be exactly parallel with these, and affords another expression for Tschermak's compound, Al_2RSiO_6. On the ground of simplicity this is preferable to the more complex expression based on the formula of spodumene. If to monticellite we assign the quadrupled formula $Mg_4Ca_4(SiO_4)_4$, and to forsterite the similar formula $Mg_8(SiO_4)_4$, diopside becomes equivalent to them in structure, with one-half the orthosilicic radicle replaced by the trisilicic Si_3O_8. The pyroxenes and the olivines thus appear to be curiously related compounds, although they are unlike morphologically.

This mode of interpreting the pyroxenes is so remote from our usual conceptions that I offer it with great diffidence. It unifies the group, however; it expresses the observed alterations of the several species; and despite its complexity it will be found to be sustained and strengthened by evidence brought out in the study of the amphiboles.

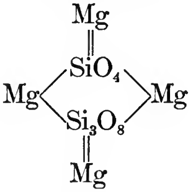
This last-named group of highly important minerals resembles the pyroxenes in composition and is explained by Tschermak in essentially the same way. Their molecular weights, however, are taken as double those of the pyroxenes, for the reason that the atomic replacements seem to occur by fourths rather than by halves. This point is exemplified by a comparison between diopside and tremolite, which, reduced to their simplest empirical formulæ, become

Diopside	$CaMgSi_2O_6$
Tremolite	$CaMg_3Si_4O_{12}$

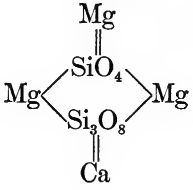
The pyroxenes, however, are somewhat heavier than the amphiboles, and from their greater density we may suppose them to have the larger molecules. Hence the formula of diopside should be a multiple of that just cited and presumably greater than $Ca_2Mg_2Si_4O_{12}$. Upon this point the phenomenon of uralitization has definite bearing. In this process pyroxene is converted into amphibole, with increase of volume and little or no change of composition. In other words, a complex molecule has been dissociated into simpler molecules—a phenomenon the direct opposite of polymerization. In the face of this evidence it is difficult to see how the current views as to the relative molecular magnitudes of pyroxene and amphibole can be maintained. The pyroxenes must form the more complex group and the amphiboles the simpler.

In the amphibole group the orthorhombic anthophyllite is the equivalent or isomer of enstatite and hypersthene. Then follows a monoclinic series, containing tremolite, actinolite, cummingtonite, dannemorite, and other minerals, all represented by the general empirical formula $RSiO_3$, with calcium, magnesium, iron, or manganese as the bivalent metal. In grünerite the salt $FeSiO_3$ exists by itself, and in richterite and astochite alkaline silicates appear. If we regard the minerals as pseudometasilicates, having molecular weights lower than the pyroxenes and with the bases replaceable by fourths, the typical amphiboles are most simply represented by formulæ like the following:

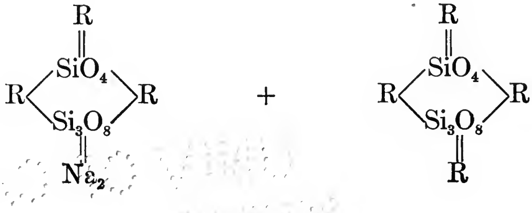
Anthophyllite.



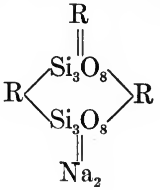
Tremolite.



Richterite becomes a mixture of salts,

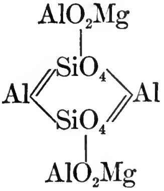


commingled in ratios near 1 : 1, and astochite is similar, but with NaH in place of Na_2. Potassium may also partly replace sodium. Another alkaline amphibole of doubtful character, waldheimite, approximates

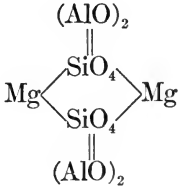


which is the formula of a trisilicate pure and simple, with R = Ca, Fe, Mg. The existence of this compound is strong evidence in favor of the pseudometasilicate theory, and, as will be seen later, it does not stand alone.

Among the amphiboles, as among the pyroxenes, aluminous and ferric compounds are common, and with these the minerals approach orthosilicate ratios. Tschermak's interpretation of these ratios is practically the same as in the pyroxene series, namely, by the assumption of molecules of the form Al_2RSiO_6 or $Al_4R_2Si_2O_{12}$. An alternative to this view is offered by Scharizer,[1] who shows that the hornblendes can be explained as mixtures of actinolite, $R_4Si_4O_{12}$, with an orthosilicate called syntagmatite $(R'_2R'')_3Al_2(SiO_4)_3$, whose ratios are similar to those of garnet. An amphibole from Jan Mayen Island approaches very nearly to syntagmatite in composition, and so also does the Canadian hastingsite. If a compound of this type is present in the amphiboles it would explain at once their alterability into epidote, micas, and chlorites, but so far as the composition of the group is concerned neither Tschermak's view nor Scharizer's is absolutely necessary. The Tschermakian molecule, however, can be written either as



or as



the latter form resembling that of tremolite, and also connecting the group still more closely with the olivines. It is also parallel to the last formula suggested for the corresponding pyroxene compound, being one-half of that formula and identical with it in type.

No amphibole is yet known which corresponds precisely in constitution to acmite and spodumene. In glaucophane we find a species,

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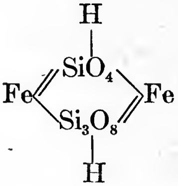
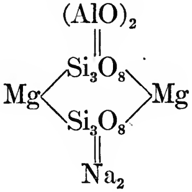
[1] Neues Jahrb., 1884, vol. 2, p. 143.

which, as a metasilicate, may be written $AlNaSi_2O_6 + (MgFe)\ SiO_3$, and in crocidolite we find another similar salt, $Fe^{\prime\prime\prime}NaSi_2O_6 + FeSiO_3$. Crocidolite alters easily, and one of the products of alteration, which has been named griqualandite, is very near $Fe^{\prime\prime\prime}HSi_2O_6$, the equivalent of acmite in general type. This last compound can be written

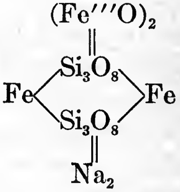


and so adjusted as an amphibole-hydrogen-acmite to the remainder of the group, but glaucophane and crocidolite are best formulated as follows:

Glaucophane.

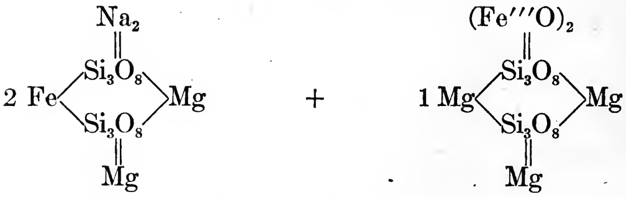


Crocidolite.



which makes them, as trisilicates, precisely equivalent in structure to the normal amphiboles. These compounds, and their corresponding orthosilicates, commingled with salts like tremolite or actinolite, give mixtures which conform in composition to the aluminous hornblendes.

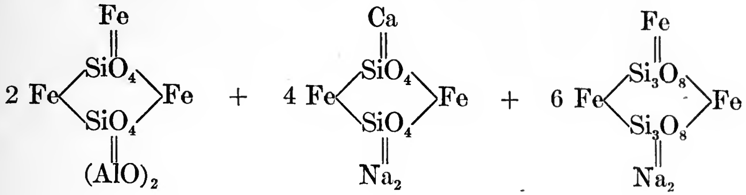
Rhodusite, which is allied to glaucophane, appears to be a mixed silicate of the following constitution:



In rhodusite the ratio of Si to O is distinctly less than 1 to 3, and the same is true of crossite, which may be written as a mixture of the two molecules

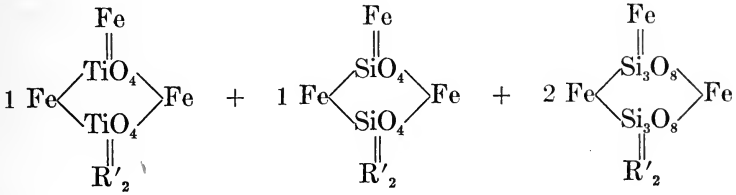
with some Al in place of Fe, and R being =Fe, Mg, Ca.

Arfvedsonite, in which R'' is mainly Fe'', is represented quite closely as a mixture of this order:



Hastingsite, soretite, and philipstadite may all be formulated in a similar way, except that they tend toward the orthosilicate end of the series. In philipstadite Si_3O_8 and SiO_4 appear in equal proportions; in the two other amphiboles SiO_4 is largely in excess. Gastaldite and riebeckite are similar species, but the analyses are not perfectly conclusive. It is, perhaps, necessary to assume the presence in these minerals of acmite-like molecules, riebeckite being empirically near $2\,Fe'''NaSi_2O_6 + FeSiO_3$. The formula of barkevikite is also uncertain.

Several minerals belonging to the group of amphiboles are characterized by the presence in them of noteworthy quantities of titanium. If this is assumed to represent an orthotitanate, the formulæ all reduce to expressions exactly similar to those given in the preceding pages. For example, the type mineral of this group is ænigmatite, to which the following formula may be assigned:



in which R' is $\frac{5}{8}$ Na and $\frac{3}{8}$ $(Al,Fe''')O$.

Cossyrite is a similar mixture of molecules, and very near

$$\begin{aligned}10\ &Fe_3(TiO_4)_2Na_2\\ 7\ &Fe_3(Si_3O_8)_2(Fe'''O)_2\\ 10\ &Fe_3(Si_3O_8)_2Na_2\end{aligned}$$

with the usual variations due to the replacement of Fe by Ca, Mg, etc., of Na by K, etc.

The other titaniferous amphiboles are also evidently variable mixtures, which, in the best analyses, are representable as follows:

Linosite.

1 $Ca_2Fe(TiO_4)_2Na_2$
1 $Ca_2Mg(SiO_4)_2(Fe'''O)_2$
2 $Mg_3(Si_3O_8)_2(AlO)_2$

Anaphorite.

1 $R_3(TiO_4)_2Na_2$
3 $R_3(Si_3O_8)_2Na_2$
1 $R_3(Si_3O_8)_2(Fe'''O)_2$

Kærsutite.

2 $CaFe_2(TiO_4)_2Na_2$
2 $Ca_2Mg(SiO_4)_2H(AlO)$
3 $Mg_3(Si_3O_8)_2(AlO)_2$

Rhönite.

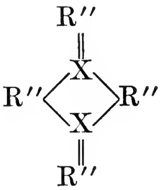
2 $Mg_2Ca(TiO_4)_2(RO)_2$
5 $Mg_2Ca(SiO_4)_2(RO)_2$
5 $Fe_2Ca(SiO_4)_2(RO)_2$

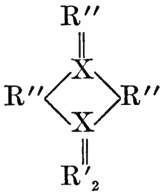
In anaphorite R = Ca, Fe, Mg, in the ratio 1 : 2 : 5; and in rhönite RO is about ⅔ AlO to ⅓ Fe'''O. Rhönite represents the orthosilicate end of the series; anaphorite shows the nearest approach to trisilicate ratios. It is evident that an indefinite number of similar molecular mixtures are possible, but all are likely to be of the same general type.

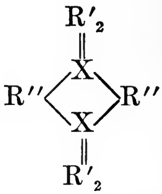
A careful study of the best analyses in the pyroxene and amphibole groups will strengthen very materially the view here developed that the species are not true metasilicates. Although in most of the analyses the approximation to metasilicate ratios is very close, there are distinct variations toward orthosilicates on one side and toward trisilicates on the other, and it is only by assuming that we have mixed silicates to deal with that all the anomalies can be made to disappear.[1] On this theory, if we represent Si_3O_8, SiO_4, and TiO_4 groups indiscriminately by the general symbol X, all the amphiboles are covered by the following typical symbols, in which R'' stands for any dyad metal, and R' for K, Na, H, AlO, or Fe'''O:

$$R''_4X_2$$
$$R''_3X_2R'_2$$
$$R''_2X_2R'_4$$

or, structurally,







In a similar way all the pyroxenes, except the acmite-spodumene group, which has the special formula discussed previously, may be represented as formed by mixtures of

$$R''_4X_4R''_4$$
$$R''_4X_4(R'''O)_8$$

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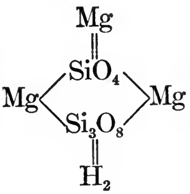
[1] This view of the constitution of the pyroxenes and amphiboles was first advanced by G. F. Becker, Am. Jour. Sci., 3d ser., vol. 38, p. 154, 1889.

which is in accordance with the theory developed by Tschermak except as to the molecular magnitude of the compounds—that is, the pyroxenes are essentially bipolymers of the amphiboles, and the character of the structure is the same for both groups. The analogy between these formulæ and those of the olivines has already been pointed out, and it is emphasized by still more evidence. Pseudomorphs of pyroxene (fassaite) after monticellite have been found at Monzoni and are well known. Furthermore, Becke[1] has described pseudomorphs of anthophyllite and actinolite after olivine, so that a connection between the two groups is clearly indicated. The tracing of this connection in a more general way would seem to offer a profitable field for investigation.

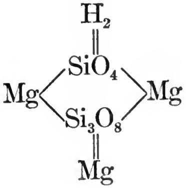
Many amphiboles contain water and some contain fluorine. These constituents are easily accounted for, being present either as univalent radicles like AlO_2H_2 and AlF_2, or with H replacing Na. Allen and Clement,[2] however, in their study of tremolite found that the mineral contained water which could be expelled continuously and therefore behaved as if it were not constitutional but in "solid solution." A study of their analyses leads to some doubt as to this conclusion. The water as determined is needed to completely satisfy the silica, and so to give rational formulæ to the different samples of tremolite which they studied. Additional investigation is plainly needed here.

Another view of the amphiboles has been developed by Penfield and Stanley,[3] who assume the presence in them of such bivalent groups as Al_2OF_2, $Al_2O(OH)_2$, Al_2O_3R'', and $Al_2O_4R''Na_2$, and also the univalent group MgF. With the aid of such assumptions they are able to formulate all the amphiboles as metasilicates. Such an interpretation of these minerals is evidently more complicated than the formulation adopted here, and it does not provide for the varieties in which the ratio Si to O is below the metasilicate requirements.

By the hydration of pyroxene or amphibole either serpentine or talc may be generated. Talc has the composition $H_2Mg_3Si_4O_{12}$, and may be written structurally like amphibole either



or



Both expressions are in accord with the fact recorded by Schneider and myself,[4] that upon the ignition of talc one-fourth of the silica is

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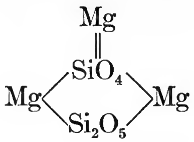
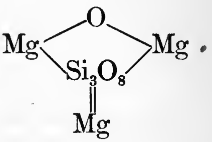
[1] Min. pet. Mitt., vol. 4, pp. 355, 450, 1881–82.
[2] Am. Jour. Sci., 4th ser., vol. 26, p. 101, 1908.
[3] Am. Jour. Sci., 4th ser., vol. 23, p. 23, 1907.
[4] U. S. Geol. Survey Bull. 78, p. 13, 1891.

set free quantitatively. This would give the ignited residue the composition shown by the subjoined alternative formulæ:



and



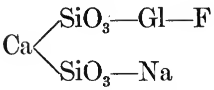
and of these the first would seem to accord the better with the remarkable stability and insolubility of the material. A metasilicate formula, $H_2Mg_3(SiO_3)_4$, is also admissible, and accords equally well with the evidence concerning talc. The pseudometasilicate expression, however, seems to be preferable in view of what is known as to the genesis of the species.

The nickel silicate, alipite, $H_2Ni_2(SiO_3)_3$, also has metasilicate ratios, but there is no further evidence as to its constitution.

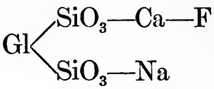
Chrysocolla is probably a metasilicate, and perhaps empirically $CuSiO_3.2H_2O$. It can not be well regarded as impure dioptase, for that mineral gelatinizes with hydrochloric acid, whereas chrysocolla does not. The species, which may be a mixture of compounds, needs careful investigation. The same is true of planchéite, to which Lacroix[1] assigns the complex formula $H_2Cu_7(CuOH)_8(SiO_3)_{12}$. Too little is known of this species to admit of any more definite formulation.

The lead silicate alamosite, $PbSiO_3$, is analogous to wollastonite and is therefore, in all probability, a true metasilicate. Agnolite, $H_2Mn_3(SiO_3)_4.H_2O$, resembles talc in its ratios, and may also be classed here.

Leucophanite, NaCaGlFSi$_2$O$_6$, is another definite species which is easily figured thus:

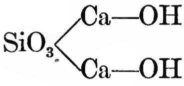


or



but between the two alternatives there is no way of deciding.

The mineral hillebrandite was interpreted by its discoverer, Wright,[2] as an orthosilicate of calcium, $Ca_2SiO_4.H_2O$. The water, however, is not given off at low temperatures, and is probably constitutional. If so, the species is a basic metasilicate,



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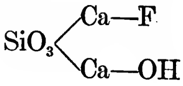
[1] Compt. Rend., vol. 146, p. 722, 1908; Soc. min. Bull., vol. 31, p. 250, 1908.

[2] Am. Jour. Sci., 4th ser., vol. 26, p. 551, 1908.

This conclusion is borne out by the fact that the mineral gives an immediate and deep rose color when its powder is moistened with phenolphthalein solution. That reaction is suggestive of the alkaline group CaOH, and a new fluosilicate, custerite, recently discovered by Umpleby and Schaller, of the Geological Survey, gives the same coloration. Custerite is represented by the formula



which is analogous to that proposed for hillebrandite.

Several other species are possibly metasilicates, although the evidence is not sufficient to warrant a definite conclusion. They are empirically—

Weinbergerite	$NaFe''_3AlSi_4O_{13}$
Spodiophyllite	$(Na,K)_2(Mg,Fe)_3(Al,Fe)_2Si_8O_{24}$
Taramellite	$Ba_4Fe''Fe'''_4Si_{10}O_{31}$

Pholidolite, a hydrous magnesian silicate, containing some potassium and aluminum also, seems to admit of no simple and satisfactory formula.

DISILICATES AND TRISILICATES.

Although the existence of the sexbasic acid $H_6Si_2O_7$ has been well established by the preparation of its esters, its metallic salts are little known and uncertain. I have already shown (see discussion of serpentine, p. 92) that a mineral may be apparently an orthodisilicate and yet be equally well explainable otherwise; and what is true for that mineral may be true for others. For the following species the orthodisilicate formulæ seem to be the best and simplest, even though they are not wholly free from objection. They fit existing evidence but are not absolutely conclusive.

The typical member of this group of minerals is the hexagonal lead silicate, barysilite, $Pb_3Si_2O_7$. The artificial compound from the slags of Bonneterre, Missouri, described by Dana and Penfield, is near this in composition, and may be $Pb_2CaSi_2O_7$. Hardystonite, $Ca_2ZnSi_2O_7$, is also typical. The pseudodeweylite of Zambonini,[1] which has the formula $Mg_3Si_2O_7.3H_2O$, is another compound of this type. The formulæ assigned to these species are merely their simplest empirical expressions. The true molecular weights are not known nor is there any available evidence to show whether or no the formulæ should be doubled or tripled.

Two other lead-calcium silicates appear to belong here. Nasonite, described by Penfield and Warren,[2] contains chlorine, and ganomalite

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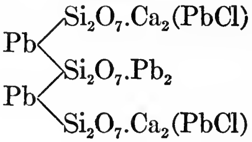
[1] Contributo allo studio dei silicati idrati, p. 88, 1908.

[2] Am. Jour. Sci., 4th ser., vol. 8, p. 346, 1899.

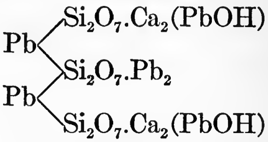
is regarded by them as the corresponding hydroxyl compound. The formulæ are simply written as follows:

Nasonite.



$$\begin{array}{l} \quad\;\; Si_2O_7.Ca_2(PbCl) \\ Pb< \\ \quad\;\; >Si_2O_7.Pb_2 \\ Pb< \\ \quad\;\; Si_2O_7.Ca_2(PbCl) \end{array}$$

Ganomalite.

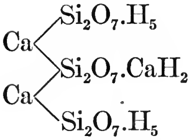


$$\begin{array}{l} \quad\;\; Si_2O_7.Ca_2(PbOH) \\ Pb< \\ \quad\;\; >Si_2O_7.Pb_2 \\ Pb< \\ \quad\;\; Si_2O_7.Ca_2(PbOH) \end{array}$$

The univalent groups —Pb—Cl and —Pb—OH are similar to other groups which have been assumed elsewhere.

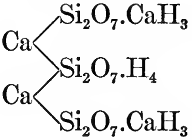
The group of zeolitic calcium silicates, okenite, gyrolite, and apophyllite, are unquestionably related to one another and are best represented as salts of $H_6Si_2O_7$. In nature gyrolite may be derived from apophyllite and apophyllite also from gyrolite, and Doelter has generated apophyllite from okenite by artificial means.[1] First, by heating okenite with potassium silicate and water to 200°, crystals of apophyllite were obtained. Secondly, by heating okenite with aluminum chloride, sodium carbonate, and carbonated water at 220°, apophyllite, analcite, and chabazite were produced. The most satisfactory general formulæ for the three species are these:

Okenite.



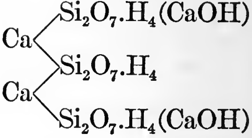
$$\begin{array}{l} \quad\;\; Si_2O_7.H_5 \\ Ca< \\ \quad\;\; >Si_2O_7.CaH_2 \\ Ca< \\ \quad\;\; Si_2O_7.H_5 \end{array}$$

Gyrolite.



$$\begin{array}{l} \quad\;\; Si_2O_7.CaH_3 \\ Ca< \\ \quad\;\; >Si_2O_7.H_4 \\ Ca< \\ \quad\;\; Si_2O_7.CaH_3 \end{array}$$

Apophyllite.

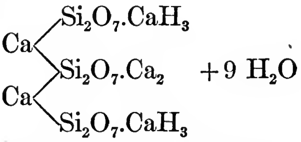


$$\begin{array}{l} \quad\;\; Si_2O_7.H_4(CaOH) \\ Ca< \\ \quad\;\; >Si_2O_7.H_4 \\ Ca< \\ \quad\;\; Si_2O_7.H_4(CaOH) \end{array}$$

In apophyllite fluorine may partly replace hydroxyl, and K may replace the univalent CaOH. With K : CaOH : : 1 : 1 the composition of apophyllite becomes

SiO_2	52.03
CaO	24.27
K_2O	6.79
H_2O	16.91
	100.00

The uncertain mineral plombierite may be a fourth member of this group, with the formula



$$\begin{array}{l} \quad\;\; Si_2O_7.CaH_3 \\ Ca< \\ \quad\;\; >Si_2O_7.Ca_2 \quad +9\ H_2O \\ Ca< \\ \quad\;\; Si_2O_7.CaH_3 \end{array}$$

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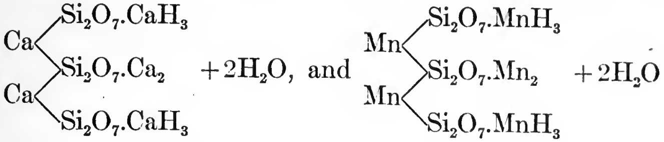
[1] Neues Jahrb., 1890, vol. 1, p. 118.

To the calcium-manganese silicate, inesite, various formulæ are assignable. By Flink it is regarded as $2(CaMn)SiO_3.H_2O$. But part of the water is stable at temperatures above 300°, and this fact is expressed by Schneider's formula $(CaMn)Si_3O_8(MnOH)_2.H_2O$. Both formulæ agree with the analyses approximately, but the analysis by Lundell is better represented by the following mixture:

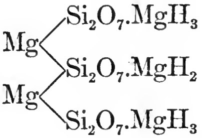


which requires the following percentage composition:

	Found, Lundell.	Calculated.
SiO_2	42.92	42.18
PbO	.73	37.44
MnO	36.31	
MgO	.37	9.84
CaO	8.68	
H_2O	10.48	10.54
	99.49	100.00

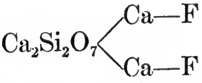
To inesite from Mexico, which contains less water than is shown above, Farrington[1] assigns the formula $H_2(Mn, Ca)_6Si_6O_{19}.3H_2O$. This formula is difficult to represent constitutionally and does not fit the analysis as sharply as is to be desired.[2]

A similar structure probably belongs to the magnesian spadaite, as follows:



Another magnesian silicate, saponite, is perhaps normally $H_4(MgOH)_2Si_2O_7$, although the analyses all show admixtures of some aluminous compound.

To cuspidine, a calcium fluosilicate, Zambonini[3] assigns the subjoined formula:



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[1] Field Columbian Mus. Bull., Geol. ser., vol. 1, p. 221, 1900.

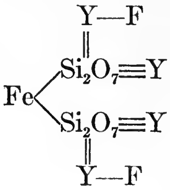
[2] See also Zambonini, loc. cit.

[3] Mineralogia vesuviana, p. 273, 1910.

An analysis of cuspidine from Franklin, New Jersey, by Warren leads to the same formula, although Palache[1] interprets it differently. Zambonini, following Groth, regards bertrandite as similar, and assigns to it the formula

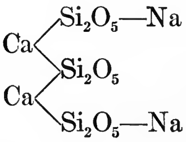
$$Gl_2Si_2O_7.(GlOH)_2.$$

In accordance with Hillebrand's analysis,[2] the rare mineral rowlandite should have an orthodisilicate formula as follows:



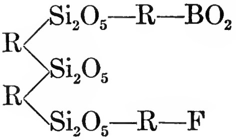
which expresses the composition of the species very closely.

Minerals corresponding to metadisilicic acid, $H_2Si_2O_5$, are rare. A few of them have already been mentioned among the alumosilicates, but only two belong here. Rivaite, described by Zambonini,[3] is a metadisilicate of calcium and sodium and is probably to be figured



which suggests a relationship with pectolite.

The rare mineral hyalotekite, which contains boron, agrees very closely with the empirical formula $R_4BFSi_6O_{17}$, if we regard the water in it as hydroxyl replacing fluorine. This can be interpreted either as a metadisilicate or as a trisilicate, with the following alternative formulæ:



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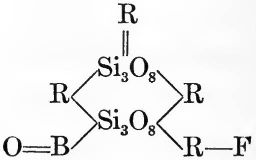

Its association with feldspar and schefferite rather favors the trisilicate formula, but the two are empirically identical. If we reduce

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[1] Am. Jour. Sci., 4th ser., vol. 24, p. 185, 1907

[2] U. S. Geol. Survey Bull. 113, p. 45, 1893.

[3] Appendice alla mineralogia vesuviana, p. 16.

Lindström's analysis to 100 per cent, after calculating the water (ignition) into its equivalent of fluorine, rejecting as impurities the traces of Al_2O_3 and Fe_2O_3, and consolidating like bases, we get the following comparison with theory:

	Found.	Reduced.	Calculated.
SiO_2	39.47	38.60	38.10
B_2O_3	3.73	3.63	3.71
PbO	25.11	25.71	26.22
CuO	.09		
MnO	.29		
GlO	.75	9.43	9.22
Na_2O	.17		
CaO	7.82		
BaO	20.08	21.32	21.59
MgO	.09		
K_2O	.89		
Al_2O_3	.18	....	....
Fe_2O_3	.06	....	....
F	.99	2.26	2.01
Cl	.06		
Ignition	.59		
	100.37	100.95	100.85
Less O	....	.95	.85
		100.00	100.00

In computing, R″ has been regarded as Ca : Ba : Pb : : 7 : 6 : 5; that is, hyalotekite is a mixture of isomorphous calcium, barium, and lead salts in the indicated ratio. The agreement between analysis and theory is as close as could be reasonably expected.

Salts of the octobasic orthotrisilicic acid $H_8Si_3O_{10}$ seem to be few in number, at least so far as present evidence goes. Two of them are silicates of nickel, namely,

Connarite	$H_2Ni_2Si_3O_{10}$
Genthite	$Mg_2Ni_2Si_3O_{10}.6H_2O$

Deweylite, according to Zambonini,[1] is equivalent to genthite, its formula being $MgSi_3O_{10}.5\text{–}6H_2O$. He shows that the so-called deweylite really represents two species, one having the formula just given, the other, pseudodeweylite, being an orthodisilicate. Pseudodeweylite has already been considered.

The complex fluosilicate, meliphanite, is also probably an orthotrisilicate, although other formulæ have been proposed for it. Zeophyl-

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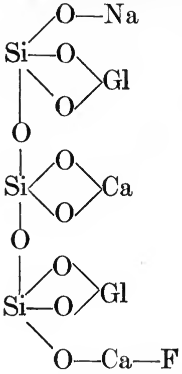
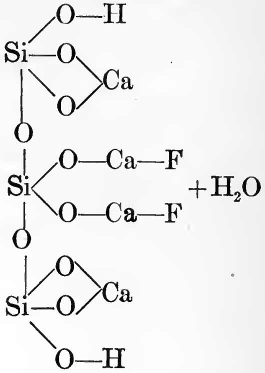
[1] Contributo allo studio dei silicati idrati, p. 88, 1908.

lite, which is in some respects allied to apophyllite, belongs in this class, and the two minerals appear to be similar in structure, thus:

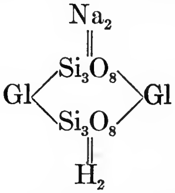
Meliphanite.



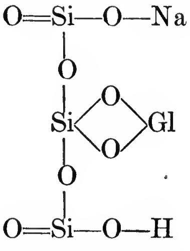
Zeophyllite.



Trisilicates of the form $H_4Si_3O_8$ are numerous in the mineral kingdom and are especially represented by the alkali feldspars and their derivatives. They are common in isomorphous admixture with orthosilicates, forming the minerals which I have classed as pseudometasilicates, and only two remain to be noted here. These two silicates, eudidymite and epididymite, have the same empirical formula, $HNaGlSi_3O_8$, which, doubled, becomes



a structure conformable to the type of several orthosilicates. The isomerism between eudidymite and epididymite is explainable by giving one species the constitution just written, whereas the other, in place of Na_2 and H_2, would have the two groups NaH. It can also be ascribed to a different linking with the oxygen of the acid, and the empirical formula $HNaGlSi_3O_8$ can be put in two forms, thus:



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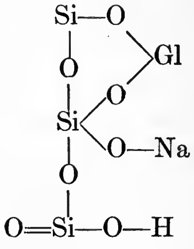


a third isomer being also conceivable. The doubled formula, however, brings out analogies with bertrandite and other species and therefore, in default of evidence, is to be preferred.

CHAPTER V.

SILICATES OF TETRAD BASES, TITANOSILICATES, AND COLUMBOSILICATES.

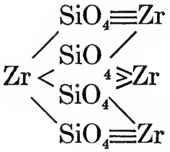
On account of their relatively small number and general scarcity, the silicates containing the tetrad metals, tinanium, zirconium, and thorium, are difficult to interpret in any satisfactory manner. Evidence exists, however, which seems to show that they are explainable by the same principles which apply to aluminum and the dyads, and that the theory of substitution from normal salts is a good working hypothesis to start from.

One definite normal salt is known in this series, the mineral zircon, $ZrSiO_4$. As with the other inorganic silicates, the true molecular weight of this compound is unknown, and it can be inferred only from a study of its derivatives. If we assume it to be represented by the polymeric expression $Zr_4(SiO_4)_4$, it contains replaceable basic atoms, and a number of other zirconium silicates fall naturally into series derivable from this as the fundamental member. In this connection the mineral auerbachite is peculiarly suggestive, for its composition is best indicated by the formula $Zr_4(Si_3O_8)(SiO_4)_3$, which goes to show an important analogy between this group of silicates and those which have been previously considered. This formula, compared with Hermann's analysis of auerbachite, gives the following results:

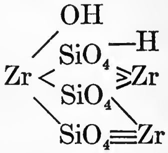
	Hermann.	Calculated.
SiO_2	42.91	42.45
ZrO_2	55.18	57.55
FeO	.93	
H_2O	.95	
	99.97	100.00

Although zircon is a very stable and definite mineral, it alters by hydration into malacone, cyrtolite, and a variety of other indefinite substances which can not as yet be interpreted with any clearness. At the same time other bases, such as lime and the rare earths, are taken up, producing mixtures of great complexity. Malacone is probably the first hydration derivative, and its relations to zircon, regarding the latter as $Zr_4(SiO_4)_4$, may possibly be as follows:

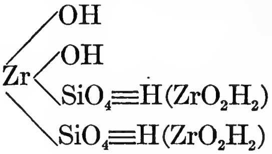
Zircon.



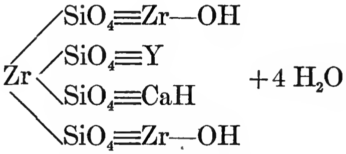
Malacone.



The original cyrtolite from Rockport is near malacone, but the cyrtolite from Colorado, analyzed by Hillebrand, approximates to



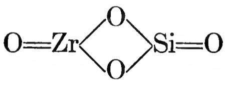
with part of the ZrO_2H_2 replaced by other bases. A number of other altered zircons or derivatives of zircon have received specific names, but their nature is more or less doubtful. Two of them, however, are interesting and may represent distinct species. The anderbergite of Blomstrand, for instance, is very near



and the alvite of Nordenskiöld, analyzed by Lindström, is well represented as a molecular mixture of two compounds,

$$Zr(SiO_4)_4(ZrOH)_4 + Zr(SiO_4)_4(GlOH)_{12}.$$

The alvite of Forbes and Dahll seems to be quite different, but the analysis of it is unsatisfactory. In Lindstrom's analysis one ZrOH group is replaced by R''', mainly Fe, Y, and Ce, and a little GlOH is replaced by Ca. Many altered zircons, like these minerals, contain rare earths in greater or less proportion, and this fact counts heavily against a common interpretation of zircon as a mixed oxide having the formula $ZrO_2 + SiO_2$, or

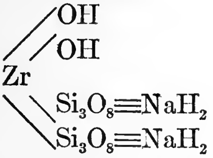


This view, which is prevalent in Germany, is based upon the close morphologic relations between zircon, rutile, and cassiterite. The chemical relations, however, are at least equally important, and a good formula must express or suggest them all. The formula here proposed for malacone is not absolutely certain. The dehydration experiments of Zambonini[1] seem to show that it may be merely a hydrated zircon, that is, a zircon containing dissolved water in variable amounts. A broader study of malacone from several distinct localities seems to be desirable.

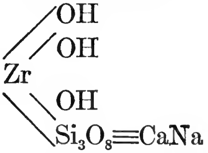
The foregoing formulæ, taken by themselves, are entitled to little consideration, but they become more significant when studied in connection with other compounds later. It will be noticed that one atom of zirconium is represented as linking four groups or radicles together, just as one aluminum atom has a similar triple function in the aluminous orthosilicates. This is practically equivalent to regarding the minerals under consideration as derivatives of a complex dodecabasic zircosilicic acid, $H_{12}ZrSi_4O_{12}$, which is at least as probable an interpretation as any other which has so far been advanced.

In eudialyte, elpidite, and catapleiite we have a group of zirconium silicates which form a highly suggestive series. Taking the simpler members first, they may be represented thus:

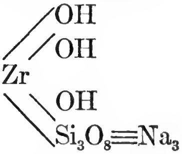
Elpidite.



Lime catapleiite.



Soda catapleiite.



Connecting these formulæ with zircon, we have the facts that Si_3O_8 occurs in auerbachite, and that at Låven, according to Brögger,[2] zircon is found both intergrown with catapleiite and pseudomorphous after it.

Here again a different interpretation of the minerals has been advanced by Zambonini,[3] who regards their hydration as extrinsic and not constitutional. To catapleiite he assigns the formula $Na_2ZrSi_3O_9.2H_2O$, which, interpreted constitutionally, becomes

$$O{=}Zr{=}Si_3O_8{=}Na_2.2H_2O.$$

The calcium-tin silicate, stokesite, is similar, and it has the formula $CaSnSi_3O_9.2H_2O$. Elpidite, according to Zambonini, is a metadisilicate,

$$Na_2ZrSi_6O_{15}.3H_2O.$$

These formulæ are legitimate and rational, and the only valid objection to them is that they fail to bring out clearly the relations between the several species and the fundamental compound, zircon.

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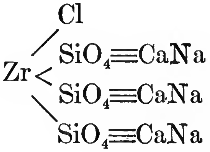
[1] Contributo allo studio dei silicati idrati, p. 72, 1908.

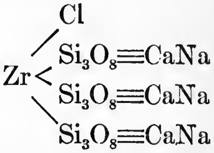
[2] Zeitschr. Kryst. Min., vol. 16, p. 105, 1890.

[3] Op. cit., pp. 54-64.

Eudialyte and eucolite are commonly regarded as metasilicates, with the compound $ZrOCl_2$ as an admixture. But that compound is not found in nature by itself, and both minerals, unlike most of the true metasilicates, gelatinize with acids. Furthermore, the analyses of eudialyte and eucolite show a considerable range of variation in the ratio Si : O, although approximating somewhat nearly to the assumed SiO_3. If now we treat eudialyte and eucolite as mixtures of trisilicates and orthosilicates, like the feldspars, scapolites, and some micas, all difficulties vanish, the chlorine becomes equivalent to hydroxyl, and the minerals fall into line with catapleiite and elpidite as the first members of the series. All varieties of eudialyte and eucolite are then interpretable as mixtures of the two molecules



and



commingled in ratios nearly but not exactly 1 : 1. Hydroxyl replaces chlorine to some extent, while iron and manganese partly replace calcium; but the ratios shown by the formulæ are constant, and the structural analogies with the allied species are perfectly clear.

The so-called "zircon pyroxenes," rosenbuschite, wöhlerite, låvenite, guarinite, and hiörtdahlite all conform to the type of expressions adopted here, although the analytical data are too scanty to yield positive conclusions. They can be given metasilicate ratios, following Brögger, by regarding the zirconium present in the form of a metazirconate. If this explanation is correct we should expect to find zirconates in nature, free from admixtures, but no such minerals are yet known. Artificial zirconates have, indeed, been prepared; but zirconium is more markedly basic than acid in its functions, and the analogy furnished by the orthosilicate zircon has been my guide in the interpretation of these species. Furthermore, the ratio Si to O in each mineral is 1 to 4 or nearly so, which places them among the orthosilicates.

The simplest of these species, and probably the most definite, are rosenbuschite and guarinite. Guarinite, which originally was described as an isomer of titanite, has recently been reexamined by Zambonini and Prior[1] and found to be identical or nearly so with hiörtdahlite, although the two minerals differ somewhat in composition. Zambonini and Prior represent guarinite as a mixed salt of calcium metasilicate and sodium zirconate, with some calcium fluoride, but the following formula, which gives the same ratios, is more probable:

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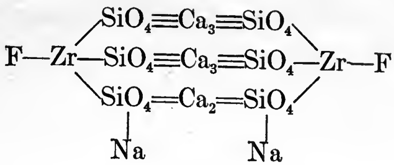
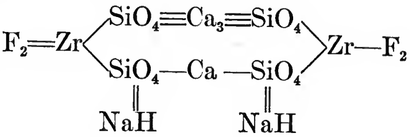
[1] Mineralog. Mag., vol. 15, p. 259, 1909.



In hiörtdahlite, as represented by Cleve's analysis, the same molecule appears, plus a less condensed molecule:

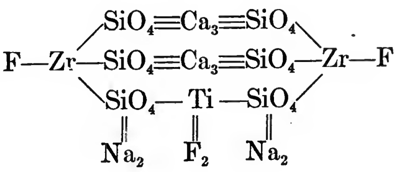


the two being commingled in the ratio 1 : 1. Hydroxyl may replace fluorine to some extent in either case.

These formulæ compare with the actual analyses as follows:

	Guarinite.		Hiörtdahlite.	
	Found.	Calculated.	Found.	Calculated.
SiO_2	30.53	31.81	31.60	30.56
ZrO_2	19.70	21.44	21.48	24.77
TiO_2			1.50	
Cb_2O_5	1.68			
Ta_2O_5	.21			
Fe_2O_3			.34	
FeO	1.91	39.36	.94	34.11
MnO	1.56		.96	
CaO	35.80		32.53	
MgO	.57		.10	
K_2O	.43			
Na_2O	6.13	5.45	6.53	6.30
H_2O			.58	.91
F	1.28	3.34	5.83	5.78
	99.80	101.40	102.39	102.43
Less O	.54	1.40	2.45	2.43
	99.26	100.00	99.94	100.00

To rosenbuschite the following formula may be assigned:

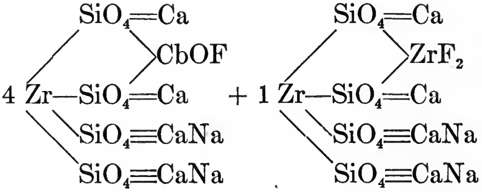


This composition compares with Cleve's analysis as follows:

	Found.	Calculated.
SiO_2	31. 36	30. 30
ZrO_2	20. 10	20. 54
TiO_2	6. 85	6. 73
Fe_2O_3	1. 00	
La_2O_3	. 33	
MnO	1. 39	
CaO	24. 87	28. 29
Na_2O	9. 93	10. 44
F	5. 83	6. 40
	101. 66	102. 70
Less O	2. 47	2. 70
	99. 19	100. 00

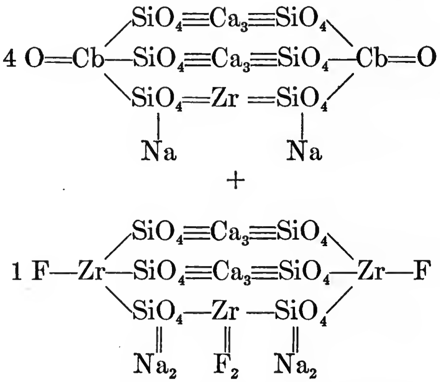
The formulation of wöhlerite is complicated by the presence of the quinquivalent element columbium, which may be either in the dyad group, ═CbOF, or in the trivalent, ≡Cb═O. This alternative leads to two possible types of structure, one of them like those immediately preceding, the other resembling that of eudialyte, thus:

I.



with small amounts of the groups R'''F replacing ZrF_2.

II.



On comparing these alternative formulæ with Cleve's analysis of wöhlerite we have:

	Found.	Calculated.	
		I.	II.
SiO_2	30.14	30.27	30.48
TiO_2	.42	18.46	19.20
ZrO_2	16.12		
Cb_2O_5	12.85	13.52	12.87
Fe_2O_3	.48	....	....
Ce_2O_3	.66	....	....
FeO	1.26	28.26	28.39
MnO	1.00		
MgO	.12		
CaO	26.97		
Na_2O	7.50	7.83	7.47
H_2O	.74	....	....
F	2.98	2.87	2.75
	101.24	101.21	101.16
Less O	1.24	1.21	1.16
	100.00	100.00	100.00

These comparisons between observation and theory are as close as could be expected when we consider the evident impurities of the several minerals. Låvenite can be formulated in a similar manner, but the result is doubtful. The mineral contains impurities which can not be easily disposed of by mere calculation. New analyses are needed on purer material.

It is worth noting, before going further, that these new formulæ for the "zircon pyroxenes" are curiously similar to those developed for garnet, epidote, meionite, spodumene, and similar minerals. In these zircosilicates the trivalent radicles $\equiv Zr—F$ and $\equiv Cb=O$ play the same part that aluminum and ferric iron play elsewhere. The analogy is suggestive but may be nothing more.

The typical silicate of thorium, thorite, or orangite is an unsatisfactory species on account of its wide variations in composition. It is commonly supposed that the mineral, as it exists in nature, has been derived from an original $ThSiO_4$ by hydration, and that $ThSiO_4$ was isomorphous with zircon. The nearest approach to the type is found in orangite, which may perhaps be regarded as a thorium cyrtolite or thorium malacone.

Yttrialite is another thoriferous mineral, which, however, seems to be a mixture of two salts. Its empirical formula is that of an orthotrisilicate, and as given by Hillebrand's[1] analysis, it is not far from

$$ThSi_2O_7R + 4Y_2Si_2O_7,$$

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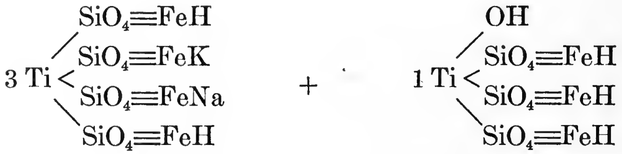
[1] U. S. Geol. Survey Bull. 262, p. 61, 1905.

R being Fe, Mn, Pb, and Ca. The second of the two compounds is analogous to thortveitite, $Sc_2Si_2O_7$. The actual mineral contains many impurities, so that its assumed constitution needs to be verified by analyses of better material, if that should ever be found. Steenstrupine is still another silicate containing variable quantities of thorium, but the analyses are discordant and unreducible to any simple formula.

Mackintoshite, a silicate of thorium and uranium, may perhaps be represented by the formula $UO_2.2ThO_2.3SiO_2.3H_2O$, and thorogummite appears to be a hydration derivative of it. Both minerals are closely related to thorite, which sometimes contains noteworthy quantities of uranium. The corresponding salts of quadrivalent uranium and thorium are probably isomorphous. Uranium functions as a hexad element in uranophane, $CaO.2UO_3.2SiO_2.6H_2O$, and the mineral is possibly a basic orthodisilicate, containing the dyad radicle UO_2. Its formula then becomes $Ca(UO_2)_2Si_2O_7.6H_2O$. Nægite is a complex zircosilicate, containing uranium, thorium, yttrium, and columbium, to which no definite formula can as yet be assigned.

To the titanium silicates astrophyllite, johnstrupite, and rinkite formulæ, like those given to zircon and its derivatives, are assignable. Indeed, this has already been done for astrophyllite by Brögger, who writes the formula $Ti(SiO_4)_4R''_4R'_4$. This seems to be the dominant molecule in astrophyllite, which, however, varies in composition. To the Colorado mineral we may more precisely give the formula



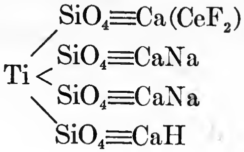
$$3\,\mathrm{Ti}<\begin{matrix}\mathrm{SiO_4\equiv FeH}\\ \mathrm{SiO_4\equiv FeK}\\ \mathrm{SiO_4\equiv FeNa}\\ \mathrm{SiO_4\equiv FeH}\end{matrix} \quad + \quad 1\,\mathrm{Ti}<\begin{matrix}\mathrm{OH}\\ \mathrm{SiO_4\equiv FeH}\\ \mathrm{SiO_4\equiv FeH}\\ \mathrm{SiO_4\equiv FeH}\end{matrix}$$

which requires the following percentage composition:

SiO_2	34.30
TiO_2	12.20
FeO	41.16
K_2O	5.36
Na_2O	3.55
H_2O	3.43
	100.00

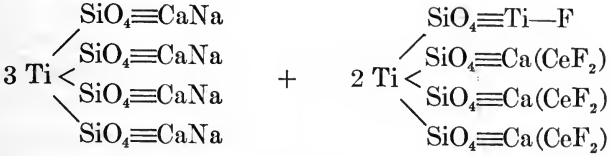
Some iron is replaced by manganese, and ferric iron, perhaps as $=Fe—OH$, is also present. In the fluoriferous astrophyllites the fluorine should replace hydroxyl.

Johnstrupite and rinkite are both fluoriferous, and both contain earths of the cerium groups. In johnstrupite, a little ZrO_2, ThO_2, and CeO_2 replace some TiO_2. For johnstrupite the expression



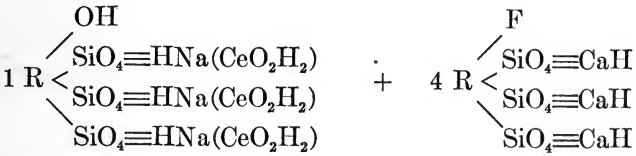
$$\mathrm{Ti}<\begin{array}{l}\mathrm{SiO_4\equiv Ca(CeF_2)}\\ \mathrm{SiO_4\equiv CaNa}\\ \mathrm{SiO_4\equiv CaNa}\\ \mathrm{SiO_4\equiv CaH}\end{array}$$

agrees well with the ratios given by analysis. In rinkite we have, with great probability, the mixture



$$3\,\mathrm{Ti}<\begin{array}{l}\mathrm{SiO_4\equiv CaNa}\\ \mathrm{SiO_4\equiv CaNa}\\ \mathrm{SiO_4\equiv CaNa}\\ \mathrm{SiO_4\equiv CaNa}\end{array} \quad + \quad 2\,\mathrm{Ti}<\begin{array}{l}\mathrm{SiO_4\equiv Ti{-}F}\\ \mathrm{SiO_4\equiv Ca(CeF_2)}\\ \mathrm{SiO_4\equiv Ca(CeF_2)}\\ \mathrm{SiO_4\equiv Ca(CeF_2)}\end{array}$$

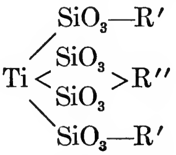
Even the complex mosandrite reduces to the same general type, agreeing very closely with



$$1\,\mathrm{R}<\begin{array}{l}\mathrm{OH}\\ \mathrm{SiO_4\equiv HNa(CeO_2H_2)}\\ \mathrm{SiO_4\equiv HNa(CeO_2H_2)}\\ \mathrm{SiO_4\equiv HNa(CeO_2H_2)}\end{array} \quad + \quad 4\,\mathrm{R}<\begin{array}{l}\mathrm{F}\\ \mathrm{SiO_4\equiv CaH}\\ \mathrm{SiO_4\equiv CaH}\\ \mathrm{SiO_4\equiv CaH}\end{array}$$

in which $R = Ce^{iv} : Zr : Ti : : 1 : 2 : 2$. For each of these species the published analyses agree well with the composition calculated from these formulæ.

Among the titanosilicates, neptunite appears to be a meta-compound, analogous in general structure to astrophyllite. Its formula, which is sharply in accord with the analysis, is



$$\mathrm{Ti}<\begin{array}{l}\mathrm{SiO_3{-}R'}\\ \left.\begin{array}{l}\mathrm{SiO_3}\\ \mathrm{SiO_3}\end{array}\right>\mathrm{R''}\\ \mathrm{SiO_3{-}R'}\end{array}$$

where $R' = Na$, K, and $R'' = Fe$, Mn.

There is still another group of titaniferous silicates which seems to be unconformable with the foregoing scheme of interpretation. Titanite, the typical member of the group, has the empirical formula $CaTiSiO_5$, for which two distinct structures have been proposed. One regards the mineral as the calcium salt of an acid, H_2TiSiO_5, analogous to $H_2Si_2O_5$, and the other treats it as a basic orthosilicate,

$$Ca{=}SiO_4{=}TiO.$$

A careful study of the recorded analyses of titanite leads me to prefer the orthosilicate expression, for the actual ratios vary in a way which indicates a replacement, sometimes of Ca and sometimes of TiO by other bases. According to the other formula, only the calcium should be replaceable. This variability of ratio is well shown by some of the varieties of titanite, such as grothite, alshedite, and eucolite-titanite, but the data are not absolutely conclusive. If, however, titanite is a basic orthosilicate, it should be classed with the orthosalts of dyad bases. On the other hand, the acid character of the titanium is suggested by the remarkable hydration derivative of titanite, xanthitane, of which the composition is approximately represented by the formula $Al\equiv Ti_2O_7\equiv H_3$.

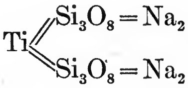
For tscheffkinite, as shown by Eakins's analyses, the composition is approximately $(FeCa)_3Ce_6Ti_4Si_6O_{32}$, but the constitution of the mineral is very doubtful. Keilhauite appears to be like titanite, with Ca or TiO replaced by $R'''OH$ or $R'''O_2H_2$, but the analyses are widely discordant.

Benitoite, having the simple and definite formula $BaTiSi_3O_9$, may be either a metasilicate or else a trisilicate,

$$Ba=Si_3O_8=TiO.$$

The trisilicate formula is analogous to that of titanite and is therefore to be preferred.

Nasarsukite is a mineral of rather uncertain relations, but apparently a trisilicate



$$Ti\begin{cases}Si_3O_8=Na_2\\Si_3O_8=Na_2\end{cases}$$

in which about one-sixth of the sodium is replaced by the univalent group —Fe═O. The ideal sodium salt compares with the analysis of the actual mineral by Christensen as follows:

	Found.	Calculated.
SiO_2	61. 63	63. 83
TiO_2	14. 00	14. 19
Fe_2O_3	6. 30	21. 98
Al_2O_3	. 28	
MnO	. 47	
MgO	. 24	
Na_2O	16. 12	
H_2O	. 29	
F	. 71	
	100. 04	100. 00
Less O	. 30	
	99. 74	

Leucosphenite, which is related morphologically to eudidymite, is probably also a trisilicate, although its formula has been written

$$Na_4Ba(TiO)_2(Si_2O_5)_5.$$

This formula is difficult to interpret structurally, and a more rational expression, which also fits the analysis fairly well, is as follows:

$$Na_8Ba_2Ti_4(Si_3O_8)_7.$$

Lorenzenite, an orthotrisilicate, appears to be a crystalline mixture of two salts, thus:

$$4\,Na_2(TiO)_2Si_2O_7 + Na_2(ZrO)_2Si_2O_7.$$

Several other minerals of more obscure character remain to be mentioned here. Molengraafite[1] is essentially a titanosilicate of sodium and calcium, which may perhaps have the empirical formula $HNa_3Ca_4Ti_3Si_4O_{20}$, if replacements and obvious impurities are left out of account. Its true character is quite uncertain. Epistolite is a complex columbosilicate, which is not far from $H_{13}Na_6Cb_3Si_5O_{27}$. Chalcolamprite and endiolite are also columbosilicates of doubtful constitution. Possibly the phosphato-silicates erikite and britholite, and perhaps also steenstrupine, should be classed with them.

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[1] See Brouwer, Centralb. Mineralogie, 1911, p. 129.

APPENDIX.

A number of well-defined silicates, of uncertain constitution, are difficult to place in any of the classes covered by preceding chapters. They may be briefly summed up as follows:

Thaumasite.—Empirical formula: $CaSiO_3.CaSO_4.CaCO_3.15H_2O$.

This can be written structurally, regarding the water as extrinsic, as in some respects analogous to wollastonite, but such a formula would lack the evidence necessary to sustain it.

Tæniolite.—A silicate of magnesia and the alkalies of uncertain composition. The one analysis of it is incomplete.

Bakerite.—A borosilicate of calcium. The empirical formula is $8CaO.5B_2O_3.6SiO_2.6H_2O$.

Roeblingite.—This species is unique in that it contains a sulphite radicle. It is regarded by Penfield and Foote as a mixed silicate and basic sulphite, $5\ H_2CaSiO_4 + 2\ CaPbO(SO_3)$.

This can be given a structural formula, which, however, would have little real significance.

Långbanite.—A silicate of manganese and iron containing antimony. Allied on crystallographic grounds to hematite and ilmenite.

A multitude of other silicates have been described as species, but without, as yet, securing full recognition. Some of these are doubtless mixtures or impure varieties of well-known minerals, but others may be ultimately established as good and definite compounds. A discussion of the analyses, without experimental investigation of the various minerals, would have very uncertain value. I therefore omit these doubtful species from consideration.

INDEX TO SPECIES.

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